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Pyrolytic Oils

Characterization and Data Development for Continuous Processing

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PYROLYTIC OILS - CHARACTERIZATION AND DATA DEVELOPMENT FOR CONTINUOUS PROCESSING

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FOREWORD

The U. S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This is a report on the characterization of oils obtained by the pyrolysis of lignocellulosic wastes and the development of processing techniques that would yield fractions suitable for industrial applications.

ABSTRACT

Pyrolytic oils produced by the pyrolysis of forestry residues in a vertical bed, countercurrent flow reactor (Georgia Tech pyrolysis process) have been thoroughly characterized. The pyrolytic oils were produced in a 500 lb per hour pilot plant and in a 50 ton per day field development facility. The overall chemical and physical properties have been determined by standard analytical techniques. The oils are dark brown to black with a burnt, pungent odor and have a boiling range of about 100°C to approximately 200°C at which point thermal degradation begins to occur. The heating values of the oils, which burn cleanly, are approximately two-thirds of petroleum fuel oil heating values. The oils, which are acidic, exhibit some corrosive characteristics. The oils are composed of a large number of oxygenated compounds which exhibit a wide spectrum of chemical functionality. Based on the results of this study, the pyrolytic oils contained phenolics, polyhydroxy neutral compounds, neutral compounds of a high degree of aromaticity and volatile acidic compounds.

A number of approaches to separating the oils into fractions, each of which would contain a predominant chemical species, were investigated on a batch basis. These approaches employed extraction techniques with water, organic solvents, aqueous alkaline solutions, and aqueous salt solutions. Based on the experimental results on a batch basis, two approaches were selected for continuous extraction experiments at the bench level with both raw oil and vacuum stripped oil. The results of these continuous extraction experiments show that these approaches are very promising as processing methods for producing oil fractions which would be useful for industrial chemical applications. Based on the results of the continuous extraction experiments, a versatile pilot plant was designed for further investigation of pyrolytic oils which would yield data for scale up of the process for a commercial plant and produce oil fractions for studies for industrial applications. Preliminary economic assessments, based on two approaches, indicate that the processing of pyrolytic oils could be economically viable. The results indicate that, for a 50 percent net return on investment, the selling price for the oil fractions would have to be in the range of 8.4 to 10.6 cents per pound which is in the same range as 9 cents per pound for coal tar creosote and well below 54 cents per pound for cresylic acid, which were quoted market prices in December, 1979. The preliminary economic assessments are encouraging for processing pyrolytic oils into fractions suitable for industrial chemical applications.

This report was submitted in fulfillment of Grant Nos. R-804416 and R-806403 by Georgia Institute of Technology under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period June 21, 1976 to March 31, 1980, and work was completed as of March 31, 1980.

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We express our thanks to the Tech Air Corporation for supplying us with oil samples from their 50 dry ton/day pyrolysis facility.

SECTION 1

INTRODUCTION

Large quantities of agricultural, forestry and municipal wastes are produced each year in the United States. The proper utilization of these materials is of extreme importance to the country so that they can be considered a resource rather than wastes. At the same time, the disposal and environmental problems these wastes create would be solved. One approach for the utilization of these materials that has received a great deal of attention in the past several years is pyrolysis. Pyrolysis of lignocellulosic or cellulosic material produces char, pyrolytic oil, water containing water-soluble organic substances, and non-condensible gases. The char is primarily carbon and can be used as a fuel or converted to activated carbon, to producer gas for use as a clean burning gaseous fuel or to synthesis gas for organic synthesis. The major components of the non-condensible gases are hydrogen carbon monoxide, carbon dioxide and methane along with minor amounts of the other hydrocarbon gases. The gas can be utilized on site as a clean burning low BTU gaseous fuel. The pyrolytic oils are clean burning with heating values approximately two-thirds the heating values of fuel oils. There is, however, a great potential for utilizing pyrolytic oils as a source of chemical materials for industrial applications and/or as a chemical feedstock. By upgrading the oils for uses of greater value than as a fuel the total economic benefit from waste materials would be of greater significance to the country. Also, the utilization of oils produced from current waste materials as a source of chemical materials would reduce the demand on petroleum materials for chemical feedstock. In order to realize the potential of pyrolytic oils as a source of materials for chemical applications, it is necessary to develop the processing technology to produce refined fractions for industrial use.

Pyrolytic oils are complex mixtures of organic compounds ranging from very volatile to high boiling materials. Many of the components are oxygenated, and the oils therefore are quite different in their chemical and physical properties from petroleum and its products. Experimental data indicate that the oil may contain as many as 200 or more compounds. The characterization of the pyrolytic oils as produced and fractions obtained from them by determination of physical and chemical properties provides data needed for the development of the technology to process the oils into more useful chemical materials.

The overall approach to developing technology for processing the oils to yield more useful fractions has been mainly with distillation techniques and separation (extraction) techniques. Distillation experiments include atmospheric and vacuum distillation, fractional distillation, steam distillation and vacuum stripping of water and volatile components. Separation techniques include extraction with water at different temperatures and an aqueous salt solution, simultaneous extraction with water and an organic solvent, extraction with alkaline solutions, and extraction of organic solvent solutions of pyrolytic oils with water. The extraction techniques show promise of having the greatest potential for processing the oil into fractions containing fairly specific chemical classes of compounds. These fractions should find ready utilization in industrial applications. Distillation offers more promise as a method for processing a specific fraction of oil into more highly refined and purified products. There are several potential approaches utilizing extraction techniques which could produce three or four oil fractions that would have potential for industrial applications. Experimental work was conducted at the bench level on both a bath basis and a continuous basis. Based on the results from the continuous extraction experiments, a pilot plant has been designed for investigating the continuous processing of pyrolytic oils. Also, the preliminary economics of processing the pyrolytic oils on a commercial scale have been evaluated.

SECTION 2

SUMMARY

Oils produced by the Georgia Tech pyrolysis process from the Tech-Air 50 dry ton/day pyrolysis facility have been thoroughly characterized. The overall chemical and physical properties have been determined by standard analytical techniques. The oils are dark brown to black and have a burnt, pungent odor. The viscosity of the oils depends upon a number of factors, such as the pyrolysis mode, the operating conditions and the amount of water emulsified in the oil. Oils which contain 10 to 15% water are relatively free flowing. The oils have heating values which are approximately two-thirds the heating values of petroleum fuel oils and burn cleanly. The oils are acidic and exhibit some corrosive characteristics.

The oils are complex chemical materials with a wide spectrum of oxygenated compounds which exhibit a variety of functional groups and wide boiling range. The chemical composition of the oils is of importance in devising processing methods for producing useful chemical fractions from the raw oils. The analytical techniques of choice for determining the chemical composition of the oils and fractions produced from them are liquid chromatography, thin layer chromatography, gas chromatography and gas chromatography/mass spectroscopy. The major classes of organic chemical species found in the pyrolytic oils investigated in this program from forestry materials were phenolics, polyhydroxy neutral compounds, neutral compounds of high aromaticity, and volatile acidic compounds.

The development of processing methods to produce fractions of the oils for potential chemical applications was focused on producing fractions which would contain predominantly a specific class of compounds. Distillation is a highly developed chemical operation and offers a possible method for processing and refining pyrolytic oils. Therefore, various distillation techniques were tested. Due to the heat sensitivity of the oils, the pyrolytic oil in the flask, after distilling about 50% to 65% of the charge, would begin to decompose. In addition, fractional distillation at low pressure did not produce any narrow cut fractions over the whole boiling range with a predominantly chemical species. Although distillation should not be considered as the initial processing step for pyrolytic oils, it should be considered as means of refining fractions of the oil produced by other processes. Some preliminary catalytic hydrogenations were carried out at about four and 20 atmospheres pressure. Based on the results of these experiments, hydrogenation should not be considered as the first processing step, but should be considered as a potential refining method for some of oil fractions produced by other processing methods.

Separation processes based on extraction techniques employing the solubility of the oil in water and various organic solvents offer a potential approach for separation of the oil into three or four major fractions, each of which would contain a predominant chemical species. Five major approaches involving extraction techniques were tested at the bench level on a batch basis. These approaches were extraction: (1) with water at different temperatures; (2) with sodium sulfate solution (salting-out effect); (3) with water and a water-insoluble organic solvent (three phase system); (4) of sodium hydroxide solutions at different pH ranges with methylene chloride; and (5) of organic solvent solutions of oil with water. The results of these extraction techniques and experiments showed promise and the approaches selected for additional work at the batch level were aqueous extraction, simultaneous extraction with water and an organic solvent and aqueous extraction of an organic solution of the oil. Both vacuum stripped and unstripped oil samples were examined by all three processes and the effects of both polar and nonpolar solvents were studied.

Based on the results of these experiments, aqueous extraction (Process No. 1) and simultaneous extraction with water and an organic solvent (Process No. 2) were selected for continuous extraction experiments at the bench level. Continuous extraction experiments were conducted with both vacuum stripped and unstripped oil samples. The data from the continuous experiments indicated the complexity of processing pyrolytic oils. The oils have a large number of compounds which exhibit a wide boiling point range and a high degree of chemical functionality and chemical nature, such as solubility, polarity, etc. The results from the continuous experiments show that both aqueous extraction, Process 1, and simultaneous extraction, Process 2 , have promise as the initial steps in processing pyrolytic oils. The insoluble oil phases from Process 1 and the MIBK phases from Process 2 did not contain any polyhydroxy neutral compounds, based on the analysis. The aqueous phases from both Processes 1 and 2 contained phenolic, polyhydroxy neutral compounds, and neutrals of high aromaticity. MIBK extraction of these aqueous phases removed the major portion of the neutrals of high aromaticity. Preliminary extraction experiments with alkali solution of the MIBK fractions showed that the phenolic fraction could be removed, which would provide two fractions, one predominantly phenolics and the other predominantly neutrals of high aromaticity. In order to obtain fractions of the oils which contain predominantly a group of compounds that are chemically similar, it would be necessary to further process the phases obtained by extraction techniques. Additional processing could include extraction steps and distillation.

In order to produce fractions of oil for chemical applications from raw pyrolytic oil from biomass, there are two major areas that need further investigation. Additional experimental work must be conducted at the small scale pilot plant level to yield suitable fractions of the oils for investigations for industrial applications and to produce data for the design of a commercial plant. In addition, the studies at the pilot plant level should include additional processing, such as distillation, of the fractions obtained by the extraction techniques. The application studies for the oil studies are necessary as each fraction would consist of a mixture of compounds. A versatile pilot plant was designed for testing at the rate of four gallons per minute, the extraction processes developed in this program. Additional processing of the fractions, such as distillation, could also be investigated with the pilot plant. The processing of pyrolytic oils with the pilot plant could be optimized to produce fractions most suitable for industrial uses as indicated by application studies and to provide the data for design of a commercial plant.

Preliminary economic assessments of the processing of pyrolytic oils were made, based on two approaches. These preliminary assessments are promising. In one approach, the average selling price per pound for the processed oil products was determined that would be necessary to provide a 15, 30 and 50 percent net return on investment. For a 50 percent return, the price range of 8.4 to 10.6 cents per pound is in the same range as 9 cents per pound for coal tar creosote and well below 54 cents per pound for coal tar cresylic acid, which were quoted market prices in December, 1979. In the other approach, two schedules of selling prices were assumed for each product in Processes 1 and 2, based on quoted market values of chemical materials which were considered to be similar. The returns on investment were very promising for both price schedules. The significance of this economic assessment is that at a relative low selling price, processing of pyrolytic oils should be economically viable and that if suitable industrial applications for the processed oil fractions can be found, processing pyrolytic oils should be very profitable.

SECTION 3

RECOMMENDATIONS

The results of this study have indicated that the processing of pyrolytic oils from wood into products suitable for commercial applications is technically feasible and the preliminary economic assessment is very promising. However, additional research and development work is needed so that this industrial potential for pyrolytic oils can be realized. The two major areas in which additional work is required are processing studies with pyrolytic oils at the pilot plant level and studies on utilization of the products in industrial applications.

It is recommended that investigations with pyrolytic oils be conducted at the pilot plant level with both aqueous extraction (Process 1) and simultaneous extraction with water and an organic solvent (Process 2). With both processes, additional processing of the initial phases should be investigated, and both raw oil and vacuum stripped oil should be tested. The objectives of this program would be to develop optimum operating conditions for producing suitable oil fractions for industrial applications, to obtain engineering data for scale up for a commercial plant, to produce sufficient quantities of oil fractions to use in a study for industrial utilization, and to obtain adequate data to make an economic analysis of the process and of the potential market for the products. A significant part of these recommendations is the investigation for potential chemical applications for the oil fractions, such as utilization in the production of resins. The objective of this phase of the program would be to establish specific applications for the oil fractions and to determine the potential markets. The results of this recommended program should provide the necessary information and data for the utilization of pyrolytic oils in chemical applications on an industrial scale.

SECTION 4

BACKGROUND INFORMATION

PYROLYSIS AND DESTRUCTIVE DISTILLATION OF WOOD

Pyrolysis is an old process and has been used industrially in the past on a batch basis to produce charcoal, pyroligneous liquor (mostly water with dissolved organic compounds), insoluble tars, and non-condensible gases. It was utilized during and after World War I in this country and was known as wood distillation. With the utilization of petroleum as a chemical feedstock, the pyrolysis process became uneconomical and is no longer practiced in this country. Various aspects of destructive wood distillation and the products have been discussed in representative literature references [1, 2, 3, 4 and 5].

The destructive distillation of wood was generally carried out as a batch process in a retort with external heat and produced the products mentioned above. The significant and important difference between the Engineering Experiment Station pyrolysis process and the old wood distillation process is that the Engineering Experiment Station pyrolysis process is a self-sustained continuous process. This is of significance because the pyrolytic oil produced in this manner from a given feed material under specific operating conditions is a reproducible product with definite physical and chemical properties. Therefore, it has potential as a feedstock for processing into other products on a commercial scale. Its potential for uses other than as a fuel warrants extensive investigation.

GEORGIA TECH PYROLYSIS PROCESS

The Georgia Tech pyrolysis process* is a continuous, self-sustained pyrolysis system which was developed over the past several years by staff members of the Engineering Experiment Station. Particular attention is devoted to this process since all the pyrolytic oil used in this investigation was produced in either one of the pilot plants on the Georgia Tech campus or at the field development facility owned by the Tech-Air Corporation. A wide variety of agricultural, forestry and municipal wastes have been processed under a variety of operational conditions with the Engineering Experiment Station pilot plant pyrolysis systems.

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*Licensed to the Tech-Air Corporation, a wholly owned subsidiary of the American Can Company.

Background Experience and Pilot Plants - Georgia Tech Pyrolysis Process

Workers at the Engineering Experiment Station, Georgia Tech, have found that pyrolysis is readily adaptable for the conversion of cellulosic and lignocellulosic wastes into useful fuels and other products. Involvement at Georgia Tech in the area of conversion of solid wastes by pyrolysis began with work in 1968 to develop a means to dispose of peanut hulls without producing the pollution problems of incineration.

The steady-flow, low temperature pyrolysis process developed at the EES involves processing of the wastes in a porous, vertical bed. Among the advantages of the process are its simplicity and its low temperature operation. These features, together, lead to a highly economical design. In addition, the system is self-sustaining and requires a minimum of processing of the wood wastes prior to pyrolysis [6,7].

The first pilot plant system, approximately five feet tall, was designed to reduce peanut hulls to a char and a combustible gas. The system built in 1968 was operated on a batch basis at first and then on a continuous basis with a manual input feed. Hundreds of pounds of peanut hulls were converted to char and off-gases during several months of testing with this equipment. Enough data were obtained to demonstrate the feasibility of developing an automated prototype converter with the vertical, porous bed design.

The large prototype, constructed in 1971, was built to operate continuously at an input feed rate of 4,000 pounds per hour. The unit was approximately 11 feet in height, and the reaction chamber was mounted on top of a water-cooled collection chamber. The feed-out was accomplished by a horizontal screw at the base of the chamber. The off-gases were treated as potentially explosive in these tests, and consequently, a system was constructed to burn the gases in an unconfined, diffusion controlled flame. Experience with these gases showed that they could be burned safely and easily by premixing and igniting in a conventional fashion. This system was operated over a period of many months, while processing thousands of pounds of feed. The reaction chamber of this converter was designed to have a minimum weight and only enough operating life to demonstrate the automatic operation of the process. This was done to reduce the overall cost of this experimental prototype. Consequently, the test program started with low temperature operation and on succeeding tests the temperature was raised. The internal structure of the reaction chamber eventually failed after approximately six months of testing as a result of the elevated temperature.

Based on the data and results from the first pilot plant unit and the experimental prototype, a third pilot plant was designed and built. This system was used to process a wide variety of feed materials to determine operating characteristics and investigate operating parameters. This system was completely rebuilt in the fall of 1975. Presently, the system includes a waste receiving bin, a belt conveyor to the converter, the converter and char handling system, an off-gas cyclone, a condenser by-pass, demister, draft fan, and vortex after-burner. The present system will process 500 to 800 lbs. waste/hour depending on the density of the feed material. Types of waste processed through the converter include peanut hulls, wood chips, pine bark and sawdust, automobile wastes, municipal wastes, macadamia nut shells, and cotton gin wastes. The pyrolytic oil used in the third phase of the experimental program was produced in this unit in 1978.

The fourth Engineering Experiment Station pyrolysis pilot plant, which is larger and more versatile, was designed, assembled and put into operation by the staff of the Engineering Experiment Station in September, 1974. This unit has a design capacity of 1,500 pounds of dry material/hour and has been used extensively to test municipal wastes, peanut hulls, and wood wastes.

Commercialization of EES Pyrolysis Process

The pyrolysis process developed by workers of the Engineering Experiment Station, Georgia Tech, was licensed to the Tech-Air Corporation in 1971 for commercialization. Tech-Air field tested pyrolysis converters at a peanut shelling plant and a lumber yard. The most extensive field testing and development program was conducted at a lumber yard in Cordele, Georgia, over a five year period. The Tech-Air field demonstration facility processed approximately 40 dry tons/day of a mixture of pine bark and sawdust and produced char, oil and noncondensed gases. The char was used for making charcoal briquettes, the oil was sold as a fuel, and the gases were being used on-site as a fuel for drying input feedstock. The char and oil can be stored and transported, and the noncondensed gases must be burned on-site. In the Tech-Air demonstration facility part of the combustion gases are used in a drier of Tech-Air design to reduce the moisture content of the feed material to less than 10%. The input feed material varies in moisture content from 30% to 55% on a wet basis, depending on weather conditions, season of year, and amount of sawdust in the feed. A number of improvements were made in the system, and the system was operated for a period of several months on a 24 hour basis with a reliability of operation at design throughput of better than 90%. An analysis of the combustion stack gases was made and comparison of these data with the EPA exhaust standards revealed that the system easily met all federal standards. The Georgia Tech pyrolysis system can be operated in a highly reliable manner with a wide range of feed materials and offers a high degree of flexibility for the conversion of agricultural and forestry residues and municipal wastes to char, oil and gas. The pyrolytic oil for the first and second phases of the experimental program was produced in this facility.

PYROLYTIC OIL FROM WASTE MATERIALS

Pyrolytic oil from different waste materials represents a potential source of feedstock for the chemical industry and/or as a source of chemicals. It has been reported that about six percent of United States consumption for oil goes for feedstock for the chemical industry [8]. On an annual basis this would amount to approximately 50,000,000 tons of petroleum. The yield of pyrolytic oil from lignocellulosic material processed by the Engineering Experiment Station pyrolysis process varies from 15 to 25 percent depending upon feed material and operation conditions. Consequently, it would require

200 to 330 million tons of dry lignocellulosic material to supply a tonnage of pyrolytic oil in the same tonnage range of petroleum used by the chemical industry. It should be pointed out that this does not imply that pyrolytic oil would be processed in the same manner as petroleum feedstock or that one ton of pyrolytic oil is equivalent on a feedstock basis to one ton of petroleum.

Accurate estimates of wastes from different sources are difficult to obtain. Based on our inquiries, particularly with the U. S. Forest Service, the amount of forestry wastes in the U. S. is estimated at 100 million dry tons annually (Heywood T. Taylor, U.S.F.S., Private Communication). This quantity of material has the potential of supplying 33 to 50 percent of the tonnage of petroleum now used by the chemical industry. The significance of these data is that from the standpoint of quantity the potential exists for pyrolytic oil from forestry wastes alone to make a significant contribution as a source of chemical feedstock. Anderson in 1972 estimated in his study net oil potential of 1.1 billion barrels of oil per year from the total organic wastes generated annually in the U. S. [9]. Tillman has recently reported that there is a potential source of approximately one billion dry tons of cull or rough trees and salvable dead trees in the U. S. [10]. The important fact that these data provide is that there are large quantities of waste material which have the potential for being converted to resources, and therefore, making a real impact on the material and energy needs of the U. S.

SECTION 5

EXPERIMENTAL--PHASE I

ANALYSIS AND CHARACTERIZATION OF PYROLYTIC OILS

The oils obtained from the pyrolysis of lignocellulosic materials are complex mixtures of organic compounds and usually contain some water. Consequently, the characterization of the physical and chemical properties of pyrolytic oils requires that one use a variety of analytical and testing techniques. Properties that are of interest in characterizing pyrolytic oils include but are not necessarily limited to density, water content, heating value, acidity, flash point, pour point, corrosiveness, filterable solids, ash, solubility in various solvents, distillation range, viscosity and elemental content, particularly carbon, hydrogen, nitrogen, sulfur and oxygen.

The identification of the chemical species and compounds and the relative quantities are data that are needed for developing methods for utilization of the oils for applications other than as a fuel oil. Among the most useful techniques for obtaining this information and data are gas, thin-layer and liquid chromatography, gas chromatography/mass spectroscopy, and infrared and ultraviolet spectroscopy.

Sources of Oil

Samples of pyrolytic oils for Phase I were obtained from two major sources: (1) the 50 dry tons/day field demonstration pyrolysis facility of the Tech-Air Corporation at Cordele, Georgia, and (2) the 500 to 800 lbs/hr pyrolysis pilot plant (Blue IV) of the Engineering Experiment Station, Georgia Tech, which is operated on campus. Some samples of oil were produced in a six inch tube furnace fitted with a condensation train and gas collection system. A complete description of this apparatus and the pyrolysis procedure has been reported [11].

The physical and chemical characteristics of pyrolytic oils depend upon the feed material, the pyrolysis process and the conditions under which pyrolysis occurs. In the old wood distillation industry, the retort batch process produced organic materials which varied from the low boiling compounds such as methyl alcohol to the insoluble tars. Continuous pyrolysis processes of today, such as the Georgia Tech process [6, 7], can be operated at steady state conditions with a given feed material to produce oils of fairly constant compositions and properties. These oils have greater potential than those from the old wood distillation industry as a source of chemical materials for industrial applications and are much more suitable feedstock for continuous processing to produce fractions of oil suitable for specific applications. For these reasons, the oils used in this investigation were mainly those produced in the continuous pyrolysis facility of the Tech-Air Corporation or in the pyrolysis pilot plant of the EES, Georgia Tech.

Samples of oil were obtained from the Tech-Air facility in July, 1976, and May, 1977. In each case, oil samples were obtained from the air-cooled condenser and the draft fan. The feed material for this facility was pine bark-sawdust, and a representative sample had the properties listed in TABLE 1.

TABLE 1. PROPERTIES OF PINE BARK-SAWDUST FEED MATERIAL

Property	Results	Method
Pinebark / Pine sawdust	70/30	Microseparation by visual means
Bulk density	213 kg/m^3 (13.3 lbs/ft^3)	- -
Moisture	10.3%	ASTM D-1762-64
Ash (weight %)	1.3%	ASTM D-1762-64
Acid Insoluble Ash (weight %)	<0.1%	-
Heating Value (dry basis)	21.2 MJ/kg (9109 Btu/lb)	ASTM D-240-74 -

Oil samples, produced in the Georgia Tech pilot plant on July 22 and 27, 1977, from pine chips and on September 16, 1977, from hardwood chips, were also used in these studies.

During the course of this investigation, samples of oil have been supplied to Dr. M. B. Polk of Atlanta University for use on E.P.A. Grant No. R 804 440 010. The oil samples provided were those obtained from Tech-Air in July, 1976, and May, 1977, and those produced in the Georgia Tech pilot plant in July, 1977, from pine chips and in September, 1977, from hardwood chips. In addition, oil samples produced in the six inch tube furnace pyrolysis facility (batch process) from a pine bark-sawdust mixture and hardwood chips were supplied.

Analytical and Test Data--

The condenser and draft fan oils obtained from the Tech Air facility in July, 1976, were characterized extensively, and the results are illustrative of the physical and chemical properties of pyrolytic oils and of the many analytical techniques and methods that can be used [12]. The data for the condenser and draft fan oils from the Tech-Air ton/day facility are given in TABLE 2.

TABLE 2. PROPERTIES OF WOOD OILS FROM TECH-AIR 50 DRY TON/DAY FACILITY

Property	Condenser Oil	Draft Fan Oil	Method
Density	1,141 kg/m^3 (9.525 lbs/gal)	1,107 kg/m^3 (9.242 lbs/gal)	-
Water content (weight %)	14.0%	10.4%	ASTM D 95-70
Heating Value (wet basis)	21.2 MJ/kg (9,100 Btu/lb)	24.6 MJ/kg (10,590 Btu/lb)	ASTM D 240-64
pH	2.9	3.3	5% Oil dispersed in water
Acid Number	75 mg KOH/g	31 mg KOH/g	ASTM D-664-58
Flash Point	111°F (233°F)	121°C (240°F)	ASTM D-93-73 -
Filterable Solids (weight %)	0.3%	0.4%	Acetone Insoluble
Copper Strip Corrosion	1	1	Classification-ASTM D-130-7
Sulfur (weight %)	0.01%	0.01%	ASTM D-129-64
Pour Point	26.7°C (80°F)	26.7°C (80°F)	ASTM D-97-66 -
Ash (weight %)	0.08%	0.03%	-
Distillation			ASTM D-86
First Drop	98°C	101°C	Group 3
10% Point	103°C	105°C	-
48% Endpoint	NA	265°C	-
53% Endpoint	282°C	NA	-
Solubility (weight %)			
Acetone	99.6%	99.6%	-
Methylene Chloride	93.5%	97.8%	-
Toluene	Slightly	Slightly	-
Hexane	Slightly	Slightly	-
Elemental Analysis (weight %)			
Carbon	51.2	65.6	-
Hydrogen	7.6	7.8	-
Nitrogen	0.8	0.9	-

Samples of the condenser and draft fan oils were stored at ambient temperature and 0°C for approximately eight months and then certain properties were determined. These data, presented in TABLE 3, show that the oils can be stored for periods of five to six months without any deleterious effects if the oils are to be used as fuels only. If the oils are to be used as a source of chemical materials, then it would be necessary to consider the effect of storage on the processing characteristics of the oils.

TABLE 3. VARIATION OF OIL PROPERTIES OVER EIGHT MONTHS PERIOD

		Stored Eight Months	
Property	Initial Value	0°C	Ambient Temperature
	Condenser Oil		
Water Content (weight %)	14.0%	20.5%	24.1%
Heating Value (wet basis)	21.2 MJ/kg (9,100 Btu/lb)	22.8 MJ/kg (9,800 Btu/lb)	21.4 MJ/kg (9,190 Btu/lb)
Acid Number	75 mg KOH/g	87 mg KOH/g	89 mg KOH/g
Viscosity*	0.275 Pa	0.350 Pa	0.175 Pa
pH	2.6	3.4	2.9
	Draft Fan Oil		
Water Content (weight %)	10.4%	15.5%	12.7%
Heating Value (wet basis)	24.6 MJ/kg (10,590 Btu/lb)	24.8 MJ/kg (10,660 Btu/lb)	24.9 MJ/kg (10,690 Btu/lb)
Acid Number	31 mg KOH/g	71 mg KOH/g	60 mg KOH/g
Viscosity*	0.233 Pa	0.079 Pa	0.475 Pa
pH	3.3	3.1	3.0

* Determined with Brookfield Viscosimeter, Model LV with Thermosel system at 25°C at 60 r/min.

Some typical properties of the condenser and draft fan oils and fuel oils are compared in TABLE 4.

Viscosity--The viscosity of liquids and its change with temperature is a significant property in the material handling and processing of liquids. A Brookfield viscosimeter, Model LV, with Thermosel system was used to determine viscosity values. The viscosity versus temperature was determined for both the condenser and draft fan oils initially and on samples which had

TABLE 4. TYPICAL PROPERTIES OF WOOD OILS AND FUEL OILS

Property	Wood Oils*		Fuel Oils†	
	Condenser	Draft Fan	#2	#6
Water Content, %	14	10.4	Trace	2
Heating Value, MJ/kg	21.2	24.6	45.7	43.2
(Btu/lb)	(9,100)	(10,590)	(19,630)	(18,590)
(Btu/gal)	(86,700)	(97,850)	(139,400)	(148,900)
Density, kg/m^3	1,141	1,107	851	960
(lb/gal)	9.525	9.242	7.10	8.01
Pour Point, °C	26.7	26.7	-18 max	18-29
Flash Point, °C	111	121	38 min	65
Viscosity, Pa's‡	0.225	0.233	0.020	2.262
Elemental Analysis				
Carbon %	51.2	65.6	86.1	87.0
Hydrogen %	7.6	7.8	13.2	11.7
Nitrogen %	0.8	0.9	-	-
Sulfur %	<0.01	<0.01	0.6-0.8	0.9-2.3

* Values obtained on oils with moisture content as reported.

† Values for fuel oils are considered typical. Sulfur will vary depending on origin of oil. Ref., North American Combustion Handbook, 1st ed., North American Mfg. Co., Cleveland, Ohio, 1952.

‡ Determined with Brookfield Viscosimeter, Model LV with Thermosel system at 25°C at 60 r/min.

been stored at 0°C and ambient temperature for approximately eight months. These viscosity curves are given in Figures 1 and 2. The viscosity versus temperature curves of samples of both oils which had been vacuum stripped for removal of water and volatiles are given in Figures 3 and 4. In order to determine the effect of prolonged heat upon the viscosity of condenser oil, samples of sealed oil were heated at 110°C for different time periods, and the viscosity was then determined for each sample. These data are presented in Figure 5. For comparison, the viscosities of the condenser oil and #2 and #6 fuel oils are presented in Figure 6.

Liquid chromatography--The wood oils are heat sensitive, reactive and contain a relatively large number of organic compounds. An analytical technique was needed which could be used in analyzing the fractions of oil obtained by the different processing methods that would not change the chemical character of the fractions. Liquid chromatography (LC) appears to be the method of choice because LC is carried out at ambient temperature, is

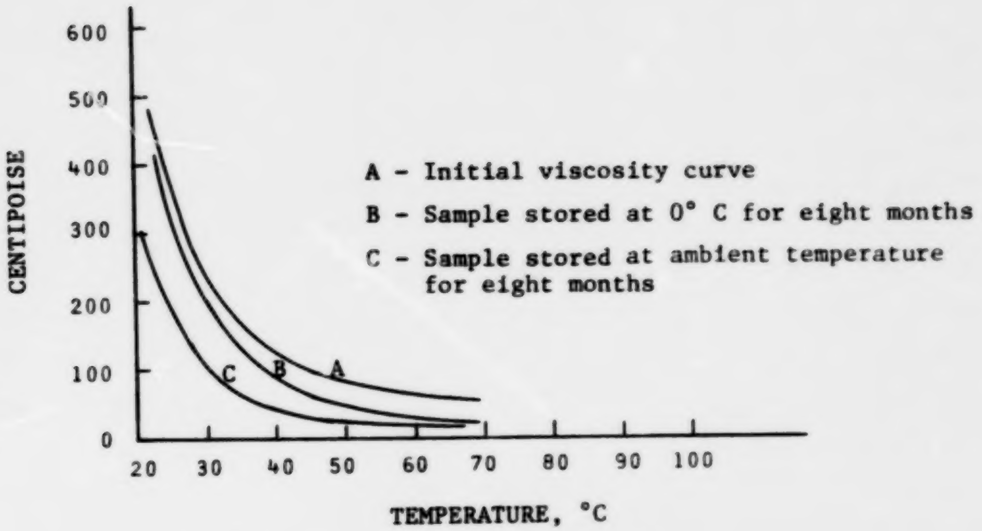

Figure 1. Viscosity of condenser oil.

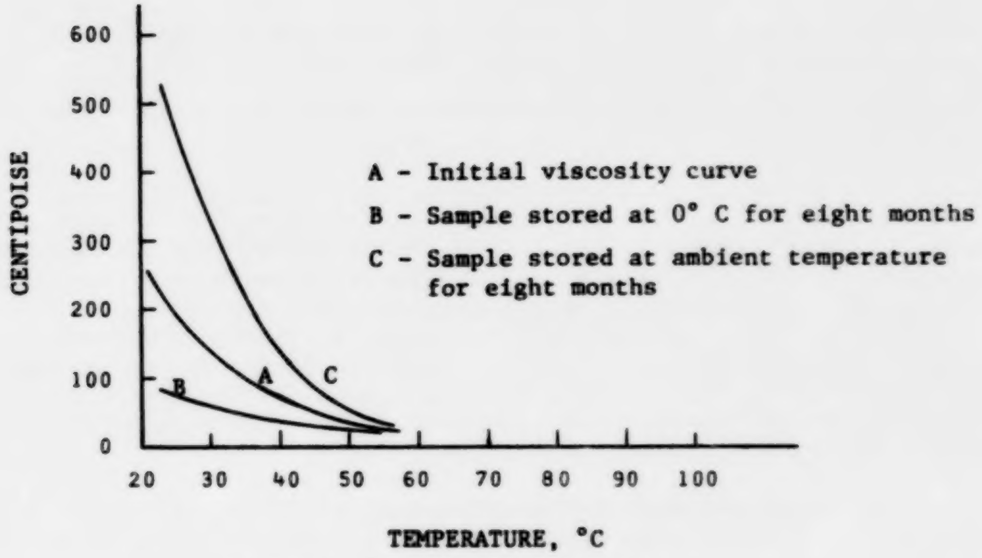

Figure 2. Viscosity of draft fan oil.

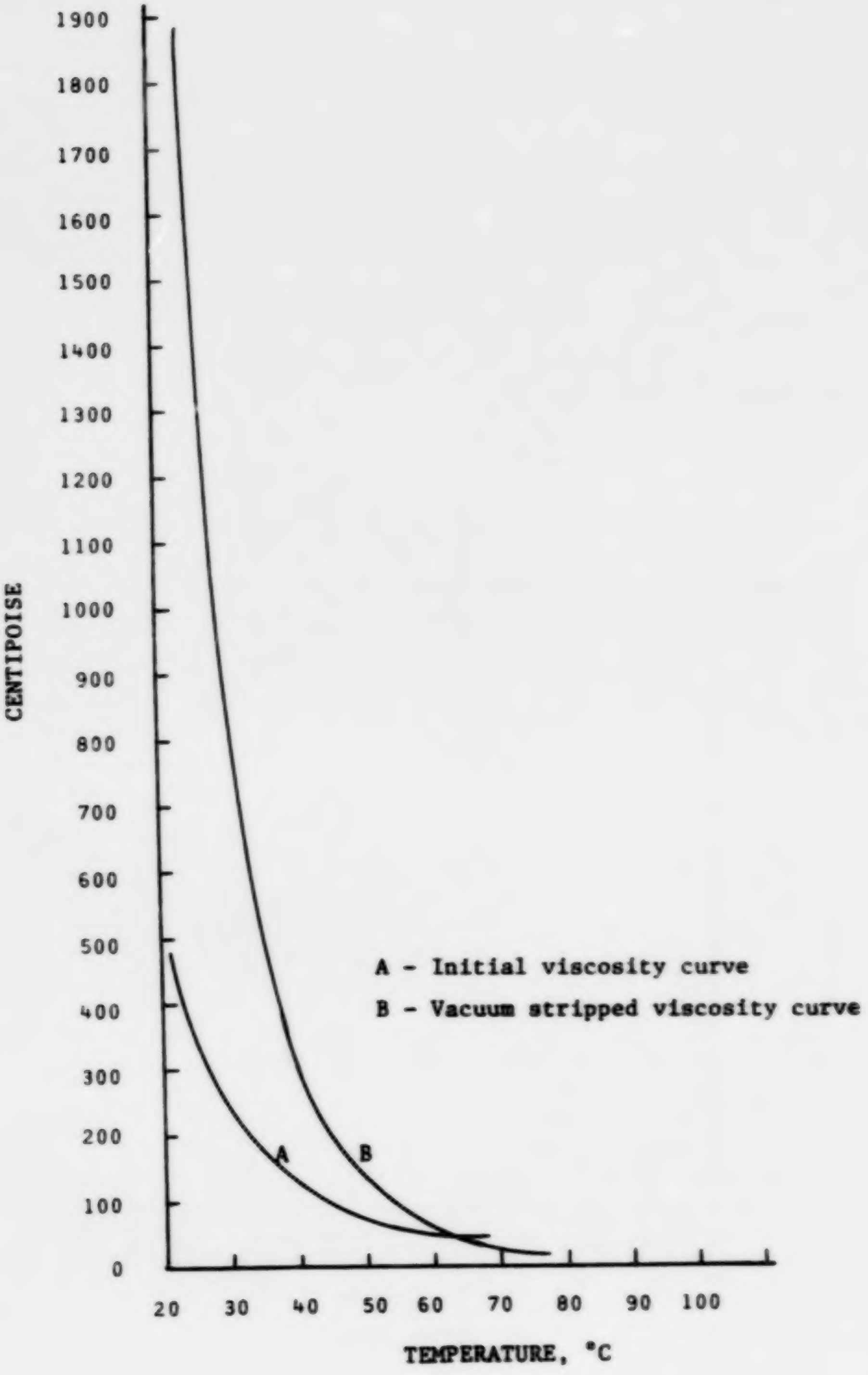

Figure 3. Condenser oil.

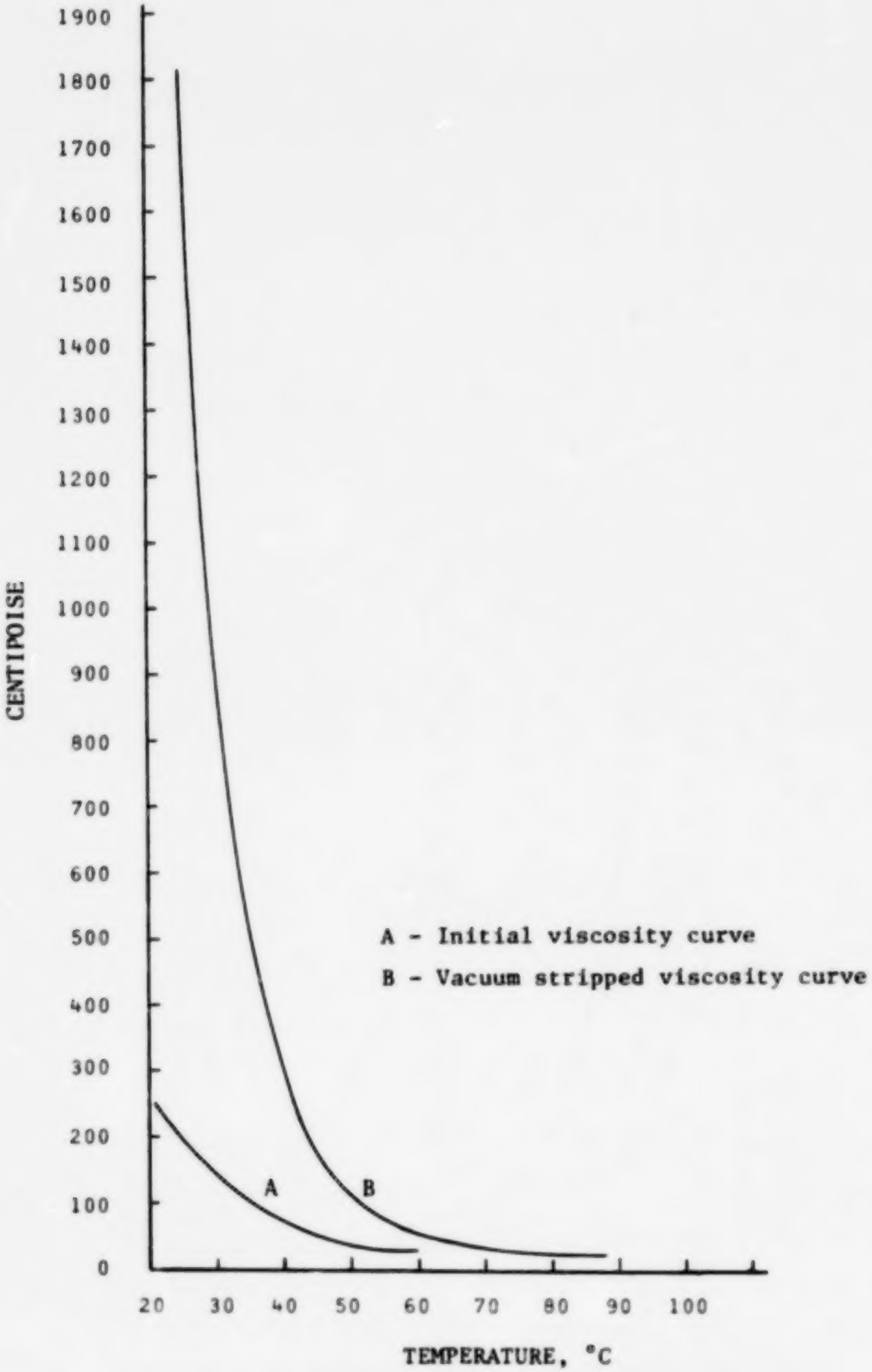

Figure 4. Draft fan oil.

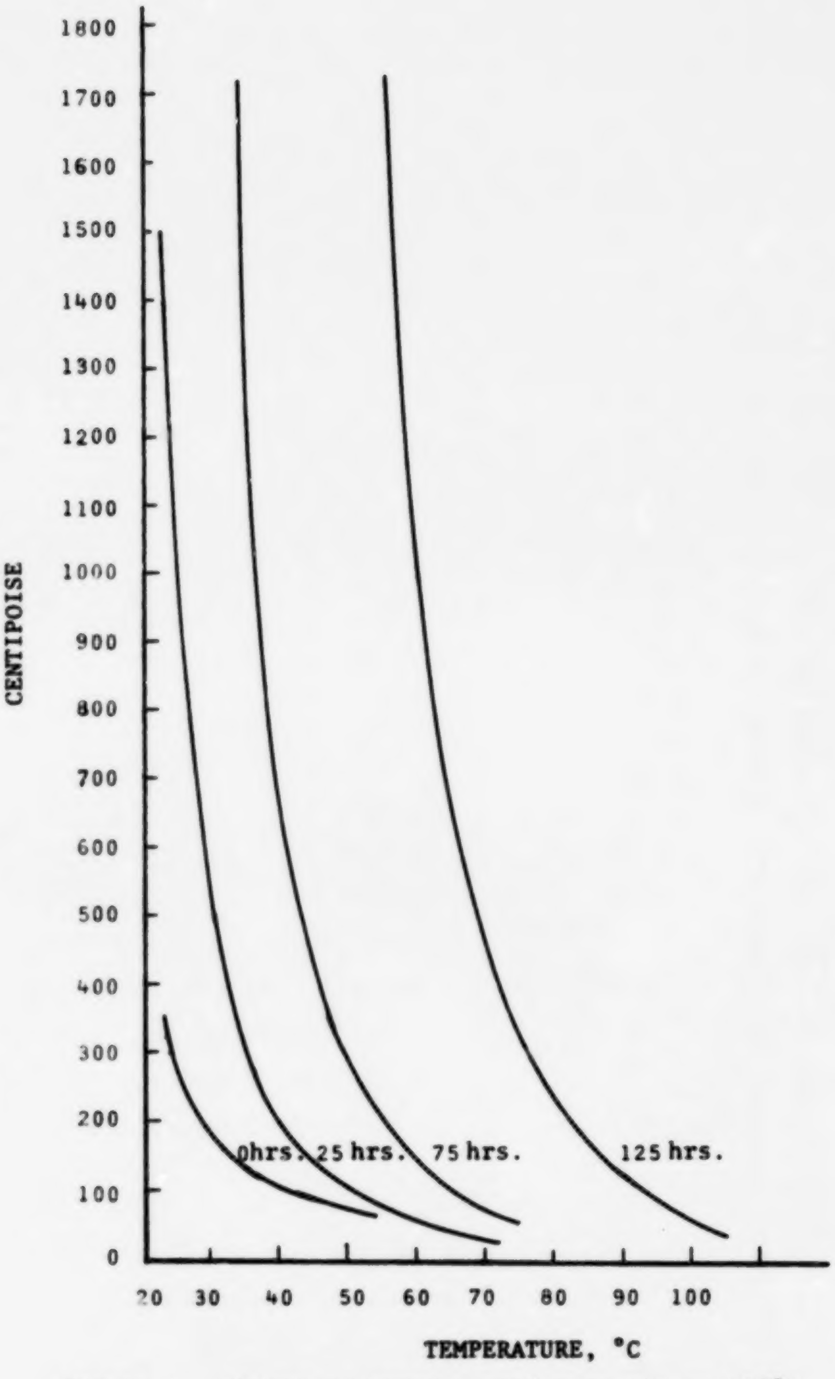

Figure 5. Effect of heating condenser oil at 110°C for different time periods on viscosity.

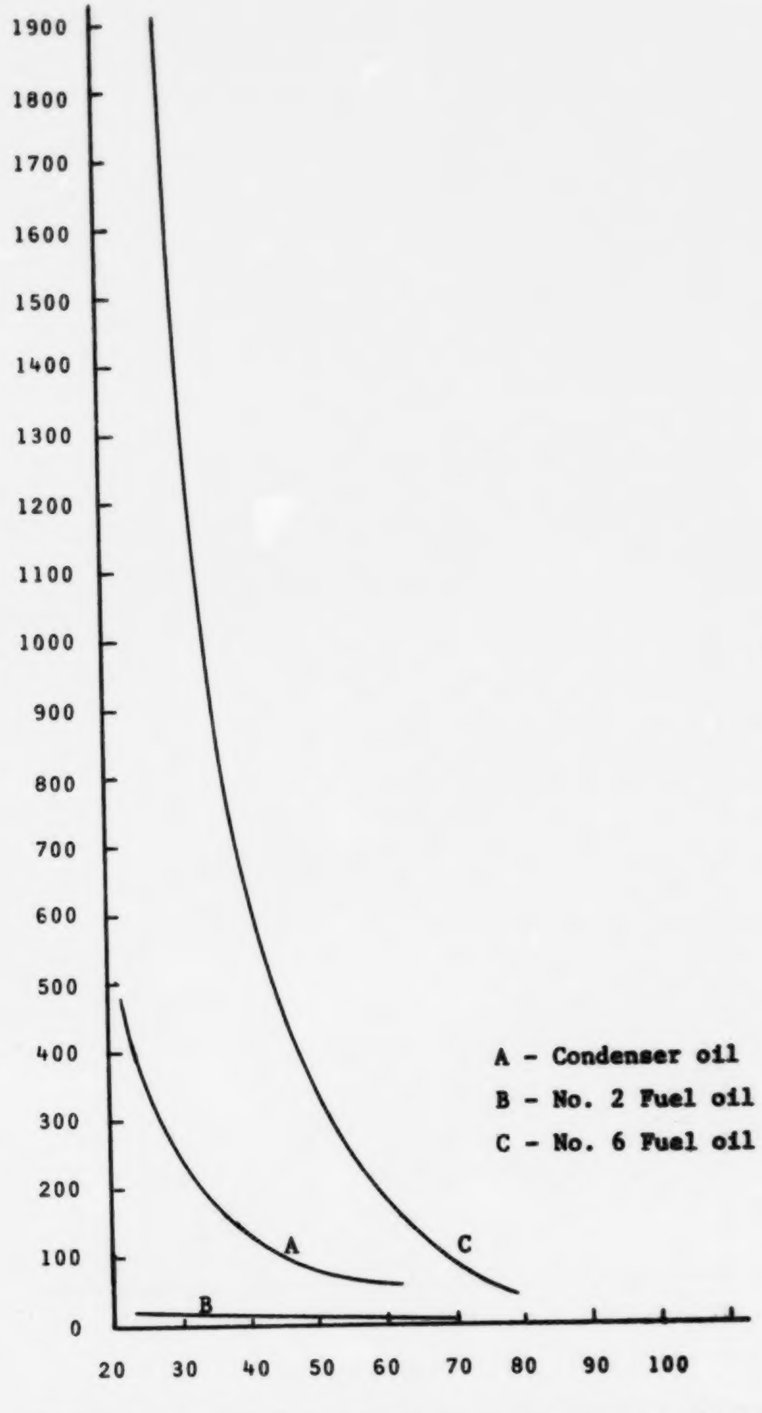

Figure 6. Viscosity curves for condenser oil (initial) and No. 2 and No. 6 fuel oils.

capable of high resolution of complex mixtures, and component detection is nondestructive. In addition, the wood oils are soluble in organic-aqueous solvent systems which are very useful in LC. The main initial objective of utilizing LC in the work with the wood oils is to provide a method to obtain "fingerprints" of the raw oil and fractions produced from it for comparison and correlation.

Testing of LC Variables--

The variables that were studied to find satisfactory LC conditions were LC columns, uv wave length, solvent gradient and solvent flow rate. The condenser oil (July, 1976) was used for testing all of these variables.

LC columns--In order to select the most suitable LC column, several columns were tested with the raw condenser wood oil (July, 1976) using one ml/min flow rate and uv detector at 254 nm. The chromatographic columns and conditions tested and the results are given below in the order in which the testing was carried out.

A. Vydac adsorption silica gel 30μ column. Solvent, 0-100% 2-propanol in isooctane, 20 min gradient 20 concave.* Results: No resolution obtained; only one large peak.
B. Partisil adsorption silica gel 5μ column. Solvent, 5-30% 2-propanol in isooctane, 20 min gradient, linear. Results: Resolution of only eight peaks.
C. Partisil PAC 5μ column. Solvent, 0-100% 2-propanol in isooctane, 30 min gradient 35 concave. Results: Resolution of 12 to 20 peaks. See Figure 7.
D. Partisil ODS 5μ column. Solvent, 10-100% acetonitrile in water, 30 min gradient 35 concave. Results: Resolution of 30-40 peaks. See Figure 8.
E. Partisil ODS 5μ column. Solvent, 10-100% acetonitrile in water, 10 to 40% with 20 minute hold, then 40% to 100% 35 concave gradient. Results: Resolution of 46-50 peaks. Total run time 60 minutes. See Figure 9.
F. Partisil ODS 5μ column. Solvent, 10-100% acetonitrile in water, 30 min linear gradient. Results: Better overall presentation of chromatogram and better resolution of later peaks without excessive runtime.

From the above results, the resolution obtained with the conditions given in D above are very suitable for our survey chromatograms and the conditions in E and F for obtaining of greater resolution.

Wavelength--The wavelengths 200, 220, 254, 280, 300, 320, 360 nm were selected and LC runs were made using constant conditions (E above) other than wavelength. The results were: (a) It was noted that many component responses appeared or disappeared with the change in wavelength; (b) no one wavelength was entirely satisfactory because at the shorter wavelengths of 200-220 nm peak resolution; (c) the longer wavelength of 300-360 nm produced sharply resolved peaks, but only a small total number of peaks

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*Term used as a dial setting for logarithmic slope control on Micrometritics LC models only.

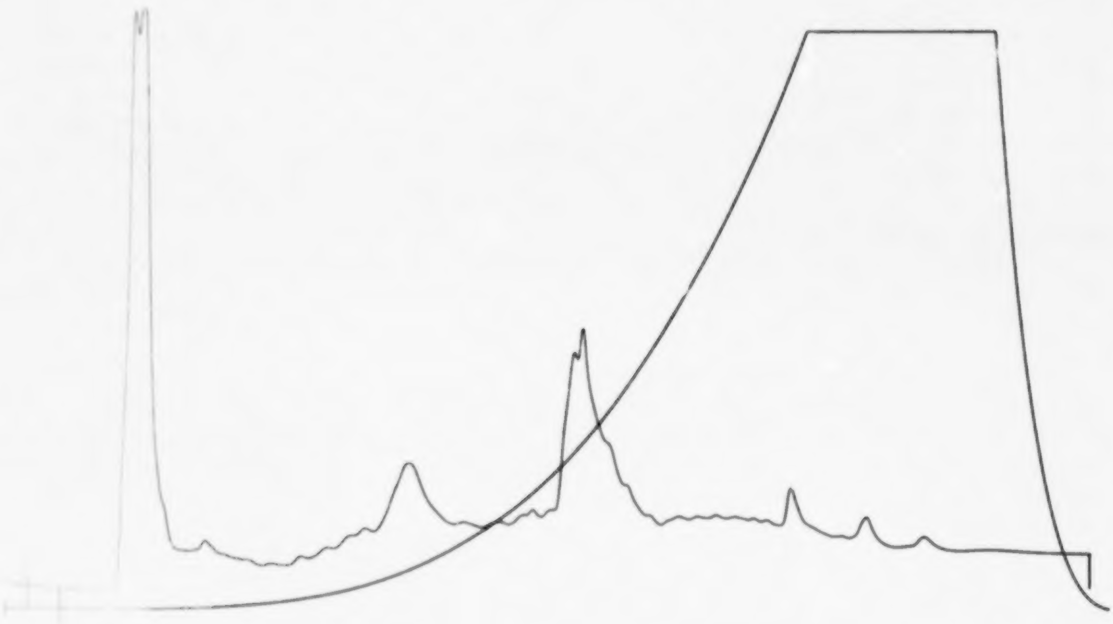


Figure 7. Liquid chromatogram of wood oil. Partisil PAC column with 0-100% solvent gradient of 2-propanol in iso-octane.

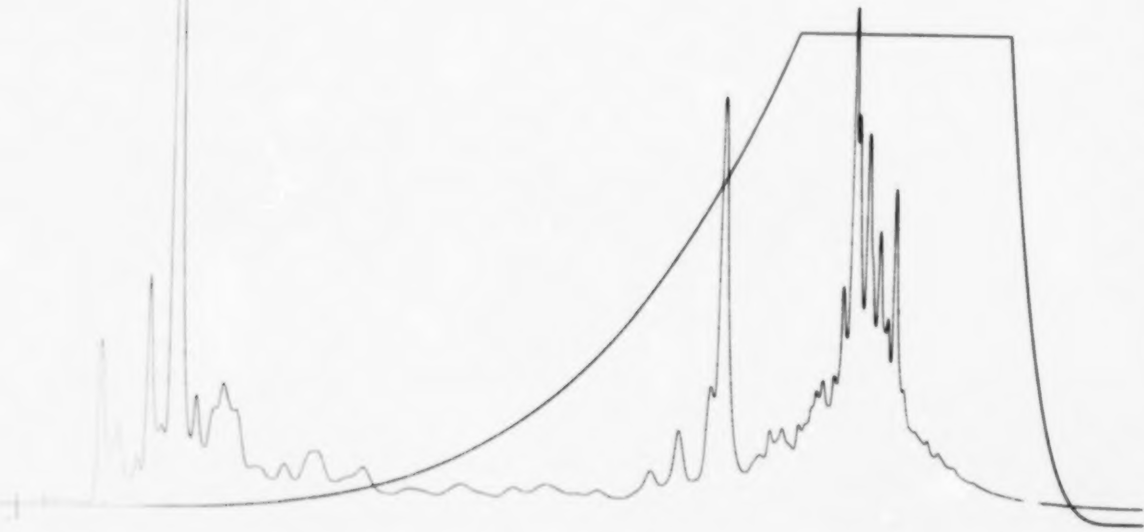


Figure 8. Liquid chromatogram of wood oil. Partisil ODS column with 10-100% solvent gradient of acetonitrile in water.

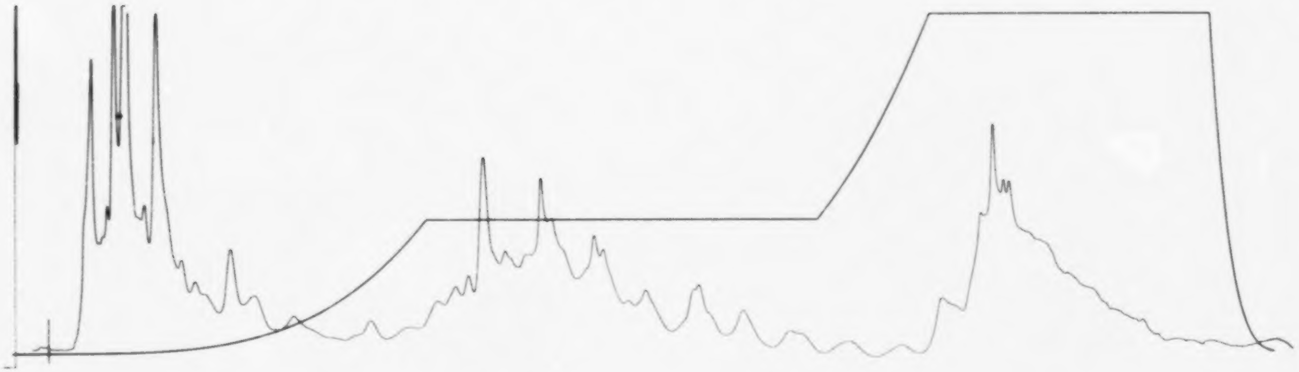


Figure 9. Liquid chromatogram of wood oil. Partisil ODS column with 10-100% solvent gradient of acetonitrile in water with 20 minute hold at 40% acetonitrile.

actually appeared; (d) and the most satisfactory results for our purposes were obtained at 280 nm with 254 nm being the alternative choice. See Figures 10 through 14 for representative liquid chromatograms of this study with condenser wood oil using conditions in E above.

Solvent gradient--The water-acetonitrile solvent system was found to be satisfactory for these wood oils. Water-methanol was tested but was unsatisfactory.

A. 10-100% acetonitrile solvent gradient with 35 concave instrument setting, 30 min long run with no solvent holds produced a short, fairly well resolved chromatogram with crowding of peaks during the last 25% of the run. See Figure 8.
B. A 10-40% acetonitrile solvent gradient with 35 concave instrument setting, and solvent hold for 20 min, then to 100% for 10 min produced a very well resolved chromatogram in 60 min. This run produces typically 50 discernible peaks from the raw condenser oil test sample. See Figure 9.
C. A gradient with 5 min solvent holds at 20%, 30%, 40%, then 10 min at 100% did not produce a better resolved chromatogram than condition B. Condition B was selected as a standard gradient with condition A being used for survey scans.

Flow rate--Liquid chromatograms were made using flow rates of 1 ml/min, 2 ml/min and 0.5 ml/min. A flow rate of 1 ml/min was selected because it produced the best resolution consistent with a practical time limitation of 1 hour per LC run.

Liquid Chromatograms of Wood Oils--

Two sets of liquid chromatographic conditions were selected for obtaining liquid chromatograms of the oil samples. Survey liquid chromatograms are obtained with the conditions given in D and greater resolution liquid chromatograms are obtained with the conditions given in E in the above discussion on liquid chromatography. Survey liquid chromatograms are presented in Figures 15 and 16 for the condenser and draft fan wood oils obtained July, 1976, from the Tech-Air Corporation. An examination of these chromatograms shows that all of the samples have a large number of components and that each chromatogram has distinctive features.

Molecular Weight Determinations of Oils by LC--

The results from the processing of wood oils from pyrolysis of wood, particularly when subjected to heat, indicate that reactions occur which produce higher molecular weight components. It is also desirable to have information on the molecular weight distribution of the raw wood oils. In an attempt to obtain some information which would be indicative of the molecular weight range of the oils and fractions of oil, the newly available size exclusion liquid chromatographic columns of silica gel with narrow pore size distribution were utilized. The column selected was a 25 cm column of DuPont SE-60 controlled size deactivated silica which has a molecular weight range of linear operation of approximately 100 to 800 Mw. Polystyrene standards of 800, 2200 and 9000 were obtained from Pressure Chemical Company,

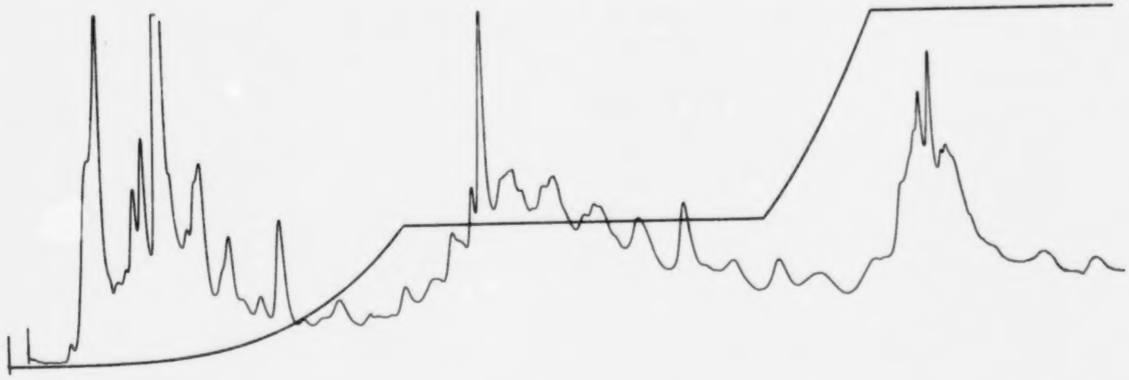


Figure 10. Liquid chromatogram of wood oil at 210 nm.

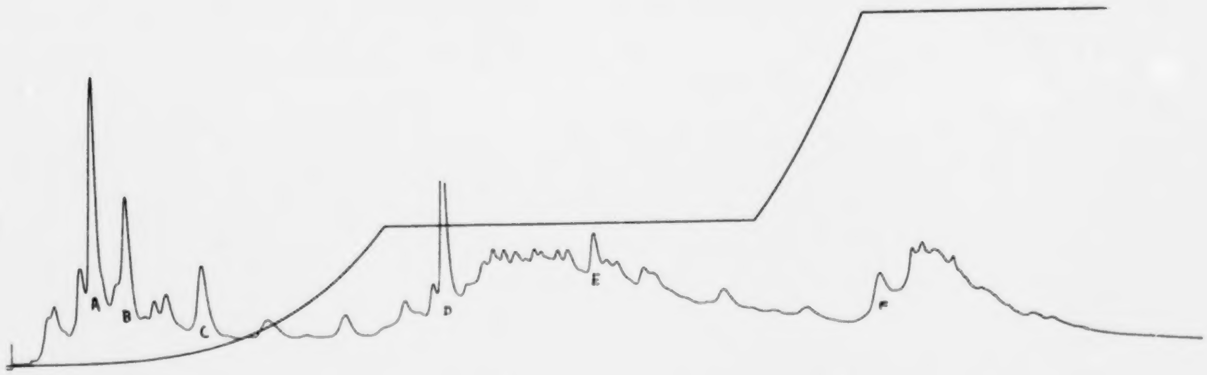


Figure 11. Liquid chromatogram of wood oil at 254 nm.

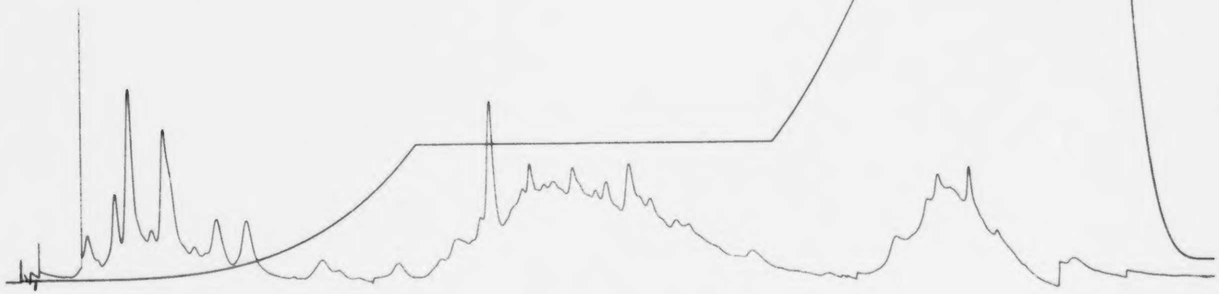


Figure 12. Liquid chromatogram of wood oil at 280 nm.

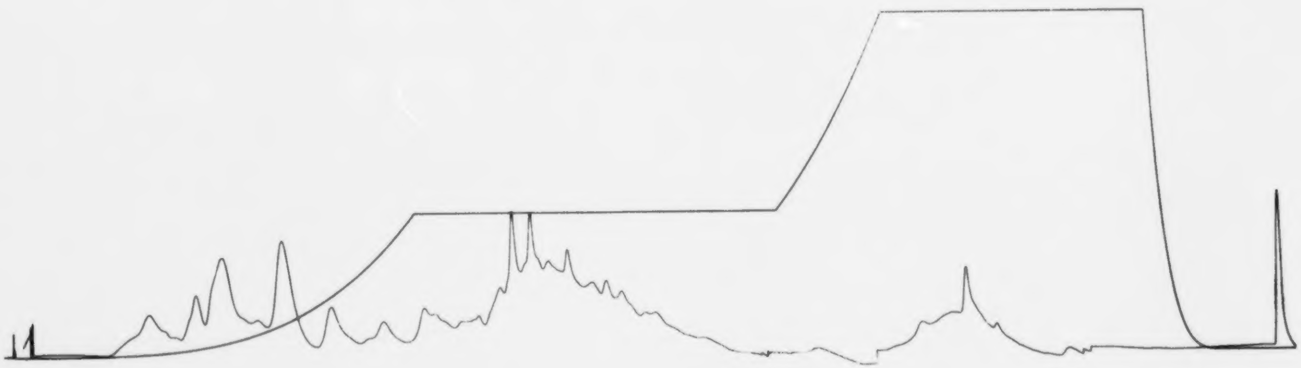


Figure 13. Liquid chromatogram of wood oil at 300 nm.

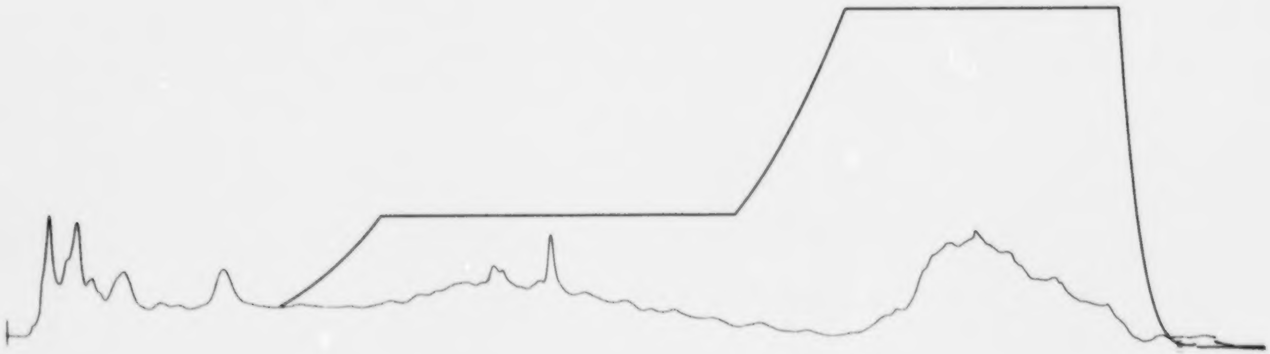


Figure 14. Liquid chromatogram of wood oil at 360 nm.

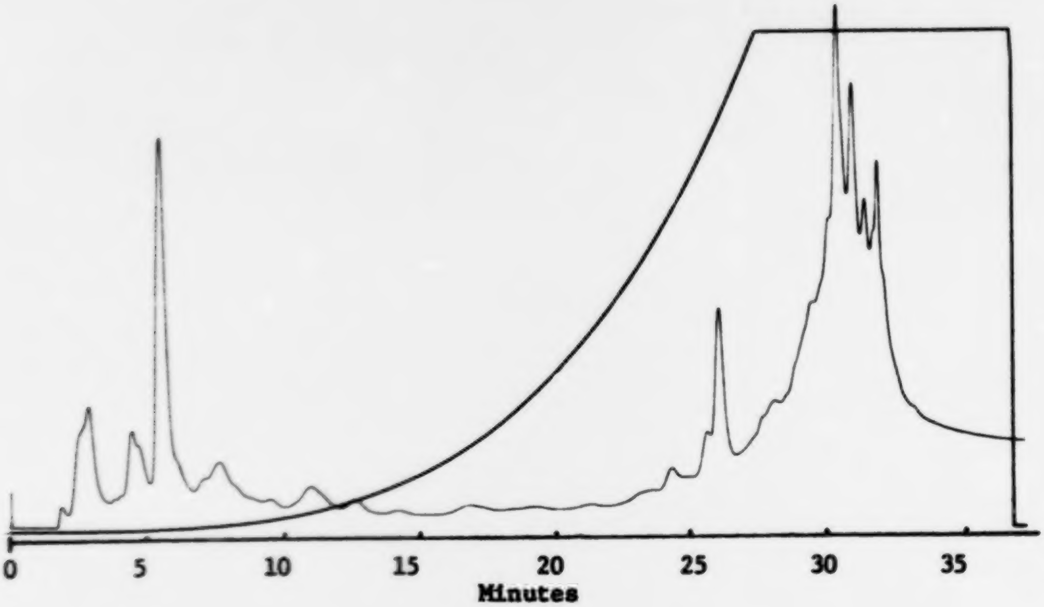


Figure 15. Survey liquid chromatogram of raw condenser oil.

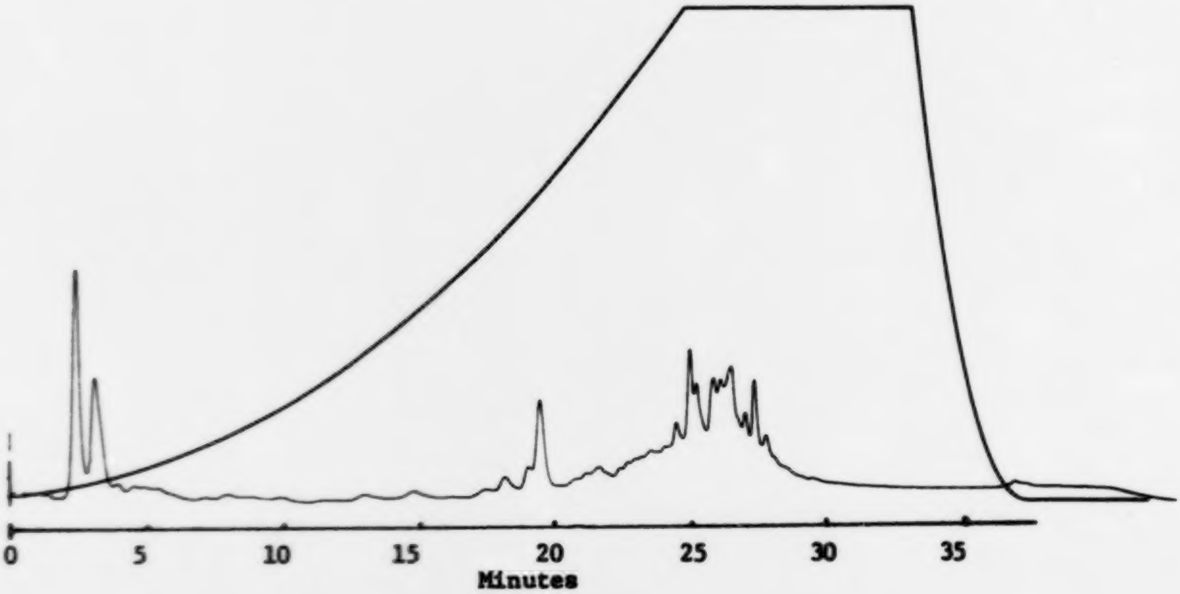


Figure 16. Survey liquid chromatogram of draft fan oil.

Pittsburgh, Pennsylvania. Benzene, molecular weight 78, was also used. In these LC runs, the solvent was tetrahydrofuran and the UV detector was set at 280 nm. The average molecular weights of raw wood oils and some oil fractions were obtained. In addition, the still bottoms from a commercial distillation of a wood oil was tested. The preliminary results from this initial work are given in TABLE 5.

TABLE 5. PRELIMINARY AVERAGE MOLECULAR WEIGHT DETERMINATIONS

Sample Description	$M\bar{w}$	Comment
Raw Condenser Oil	160	-
Raw Draft Fan Oil	150	-
Still Bottoms from Atmospheric Distilled Oil	150	-
Vacuum Spinning Distillation		
Fractions 1-4 (combined)	100	-
Fraction 8	80 and 120	Two Main Components
Fraction 12	150	-
Still Bottoms Steam Distilled Oil	150	-
Still Bottoms from Commercially Distilled Oil*	112 - 9000	Broad $M\bar{w}$ Distribution

* Obtained from Tech-Air Corporation

Gas Chromatography

Gas chromatography (GC) offers an excellent technique for analyzing complex mixtures of organic compounds. The apparent disadvantage in analyzing wood oils (produced by pyrolysis) by GC is the heat sensitivity of some components in wood oils and the possible effect of the heat on these components during GC analysis. Recognizing this possible constraint, GC should be useful for analysis for fractions containing more volatile components, for water soluble components and for fractions obtained in experiments designed to separate pyrolytic oils into fractions containing a major chemical class of compounds.

In addition, it was considered appropriate to do some preliminary analysis of the raw wood oils because of the powerful analytical capability of GC. The instruments used were a Perkin Elmer Model 900 with a flame ionization detector with dual column and temperature programmed capability, and a Perkin Elmer Model 990 with thermal conductivity detector, dual column, and isothermal oven.

The objectives of this gas chromatographic work are to be able to resolve the low molecular weight components in the aqueous phases of various distilled fractions, to resolve the more volatile components of the oils and fractions of oil, and to analyze the higher molecular weight components of the relatively water-free wood oils and fractions obtained from the oils. To date, two columns were selected from several GC trial runs with the raw condenser oil and a distilled aqueous fraction. The list of columns and conditions that have been tried are given below.

Initial Conditions: P.E. 900 FID detector. Carrier gas, N_2 at 20 ml/min temperature program as shown.
P.E. 990 T.C. detector. Helium carrier gas at 20 ml/min; isothermal oven.
Samples tested were raw condenser oil and aqueous distillation fraction.

Column 1. Porapak Q, 9' x 1/8", with 1' x 1/8" Porapak Q precolumn to retain and prevent the heavy organics from entering the main column. Oven 120°C, injector 200°C, thermal conductivity 225 ma, Helium carrier at 20 ml/min. Results: The determination of water, lower alcohols, formaldehyde and acetone was accomplished.

Column 2. 3% Poly-m-phenoxylene on 80/100 Chrom P DMCS, 6' x 1/8". Injector 250°C, manifold 250°C, oven 130° - 200°C @ 8°/min. FID, N_2 at 20 ml/min. Results: moderate resolution of sample, 18 peaks, from raw oil.

Column 3. 10% Dow Corning High Vacuum Grease on 80/100 AWFB-DMCS 10' x 1/8". Injector 340°C, oven 150° - 350°C @ 10°/min FID, N_2 20 ml/min. Results: 48 peaks minimum resolution from raw oil.

Column 4. 1% Polyphenylether (6 rings) on 80/100 AWFB-DMCS 3' x 1/8". Injector 250°C, manifold 250°C, oven 130°C @ 10°/min FID, N_2 20 ml/min. Results: moderate resolution of sample, 23 peaks from raw oil.

Column 5. 10% SP-2100 on 80/100 Suppelcoport 6' x 1/8". Injector 250°C, manifold 250°C, oven 60° - 250°C @ 5°/min. FID, N_2 20 ml/min. Results: Better resolution of components; 58 - 52 peaks from raw oil with better baseline separations.

Column 6. 10% Carbowax 20 M on 80/100 Supelcoport 6' x 1/8". Injector 250°C, manifold 250°C, oven 60° - 250°C @ 5°/min, FID, N_2 20 ml/min. Results: Good resolution of low boiling compounds.

DISTILLATION OF PYROLYTIC OILS

Distillation offers a possible method for processing and refining pyrolytic oils obtained from lignocellulosic materials to yield more desirable and useful products of greater value, and thereby, increasing the economic value of these oils. The oils contain a wide spectrum of organic compounds including a large number of aromatic compounds. Because of the wide variety of organic compounds in the oils, they offer the potential as a source of chemical materials which should find many industrial applications.

A number of distillation experiments were conducted with oils obtained from the Tech-Air Corporation. These include distillation at atmospheric pressure and at 0.2 - 0.4 mm mercury, fractional distillation at reduced pressure, steam distillation and vacuum stripping. The data from these experiments have been reported [12]. Representative liquid chromatograms are presented in Figures 17, 18, 19, 20, 21, 22, and 23.

HYDROGENATION

Oil samples from different sources were hydrogenated catalytically to determine how much hydrogenation would occur and the effect of hydrogenation on the stability of the oil and to prepare samples for use in various separation schemes. Hydrogenation was carried out in a Parr Model 3911 hydrogenation apparatus which provides for agitation by shaking and can be used at pressures up to approximately 4 atmospheres. One hydrogenation was conducted at atmospheric pressure utilizing a recycling of the hydrogen in a stirred flask containing the sample and catalyst. Anhydrous ethanol was used as a solvent, and five percent palladium on activated carbon or five percent platinum on activated carbon was used as a catalyst. The results from the hydrogenations with the low pressure Parr apparatus and at atmospheric pressure are given in TABLE 6.

The data from hydrogenations 5, 6 and 7 show that the Pd catalyst performs better as the hydrogen absorbed is approximately fifty percent greater in one-third of the time used for the hydrogenations with Pt. The data from hydrogenation 4 show that hydrogenation at atmospheric pressure is too slow. Examination of the data from hydrogenations 5, 8 and 9 shows that the Blue IV fan oil from both hardwood and pine chips absorbed approximately the same amount of hydrogen under similar conditions, whereas the Blue IV composite hardwood oil adsorbed 2.2 times as much hydrogen as the Blue IV composite pine oil. It is of interest that the vacuum stripped hardwood oil, hydrogenation 11, absorbed 1.56 as much hydrogen as the vacuum stripped pine oil, hydrogenation 10.

Hydrogenations are frequently carried out at a much higher pressure than those discussed above. In order to test a higher initial hydrogen pressure, a Parr Model 1108 calorimeter bomb was connected to a high pressure hydrogen reservoir (lecture bottle size) utilizing a Parr oxygen bomb filter hose assembly and stainless steel tubing. Agitation was provided by means of a magnetic stirrer. Three hydrogenations were carried out with this apparatus with vacuum stripped Blue IV fan pine oil. In each hydrogenation, two grams of five percent palladium on activated carbon and 100 ml of absolute ethanol were used. The hydrogenated oil was recovered by removal of the catalyst by filtration and then vacuum stripping of the ethanol at 2 mm pressure. The results of these three hydrogenations are given in TABLE 7. An examination of the data shows that the hydrogen absorption is the same for each experiment and that the samples absorbed approximately seventeen percent more hydrogen than the same sample at approximately 4 atmospheres (hydrogenation 10 TABLE 6).

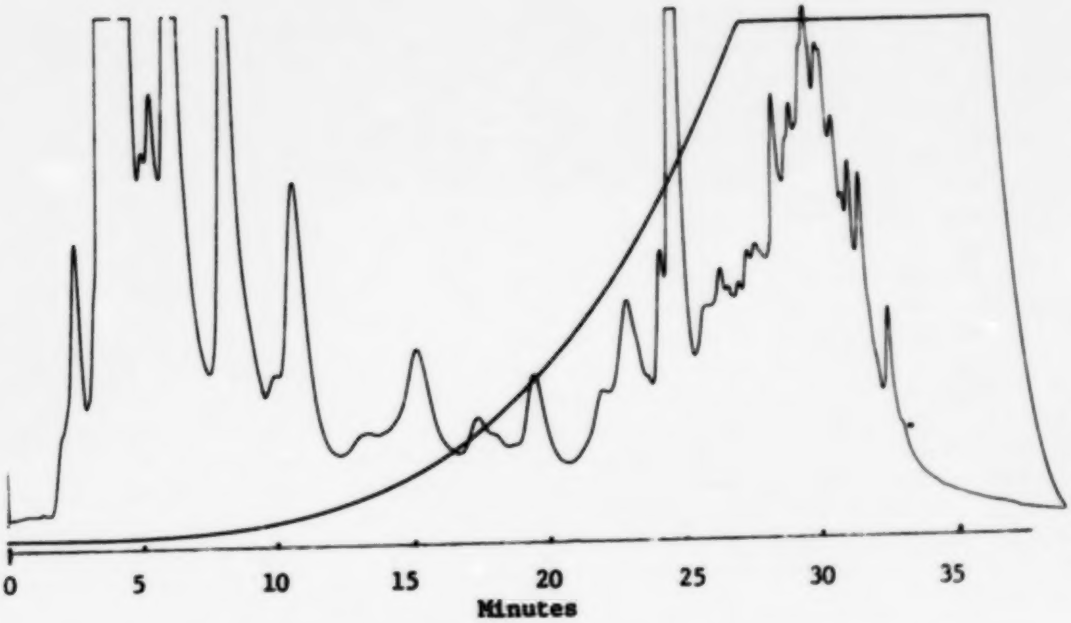


Figure 17. Survey liquid chromatogram of combined fractions from vacuum distillation.

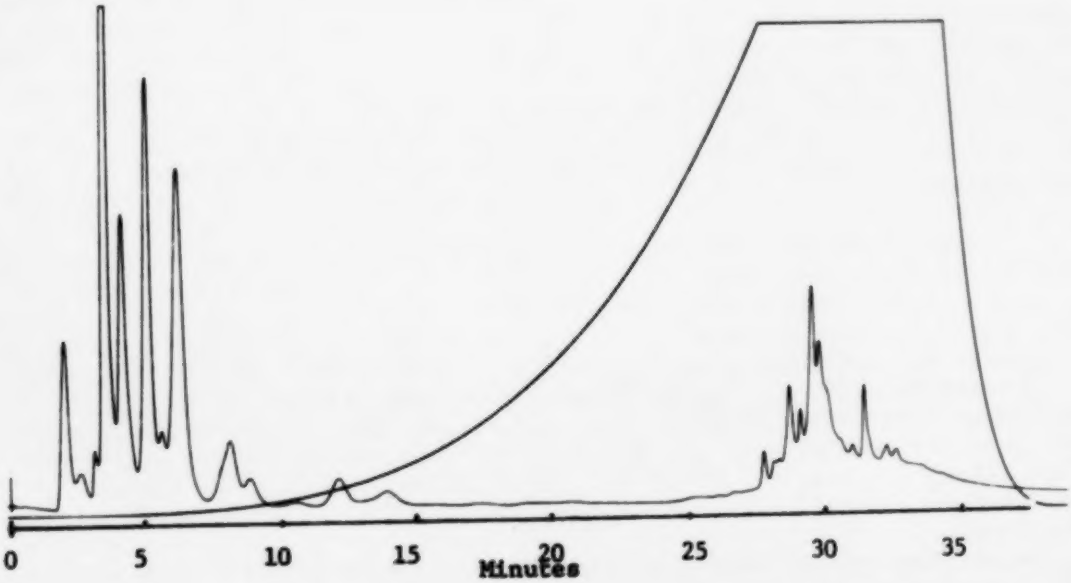


Figure 18. Survey liquid chromatogram of spinning band fraction one.

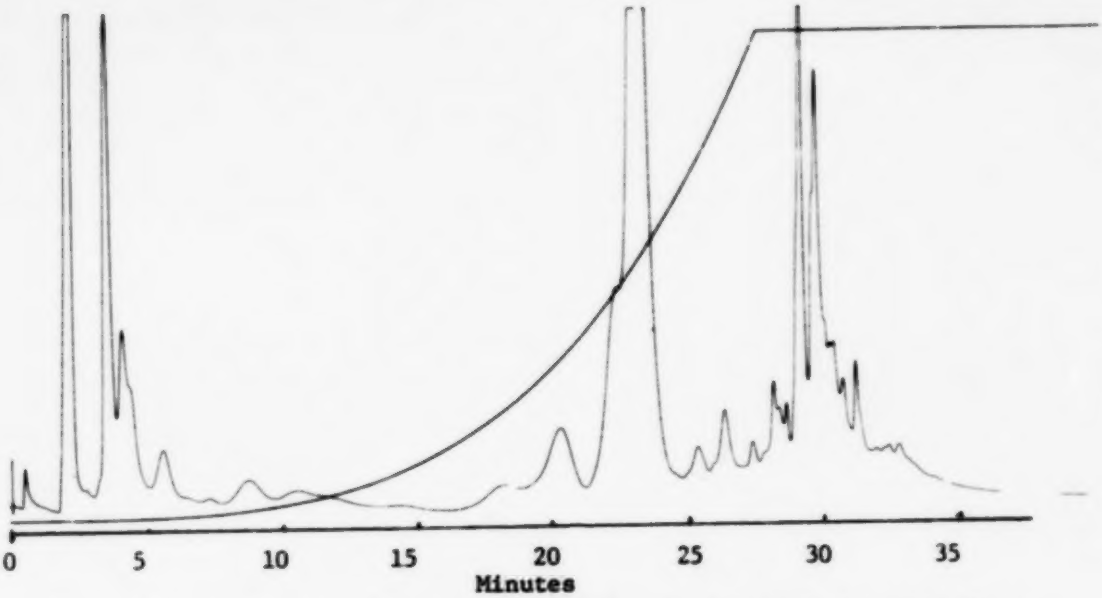


Figure 19. Survey liquid chromatogram of spinning band fraction five.

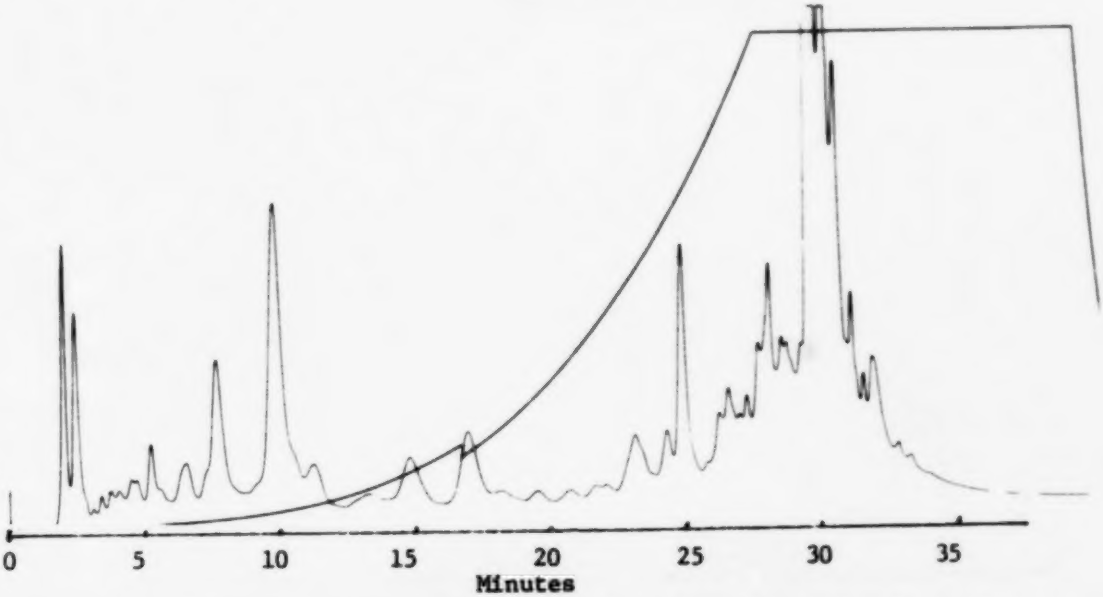


Figure 20. Survey liquid chromatogram of spinning band fraction nine.

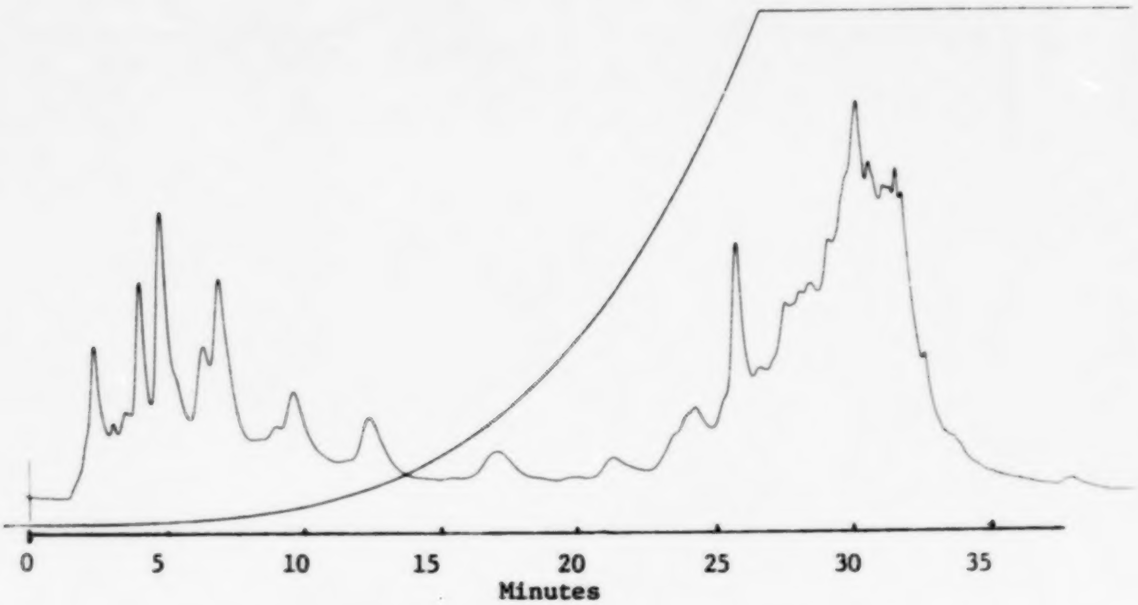


Figure 21. Survey liquid chromatogram of condenser oil vacuum stripped without heat.

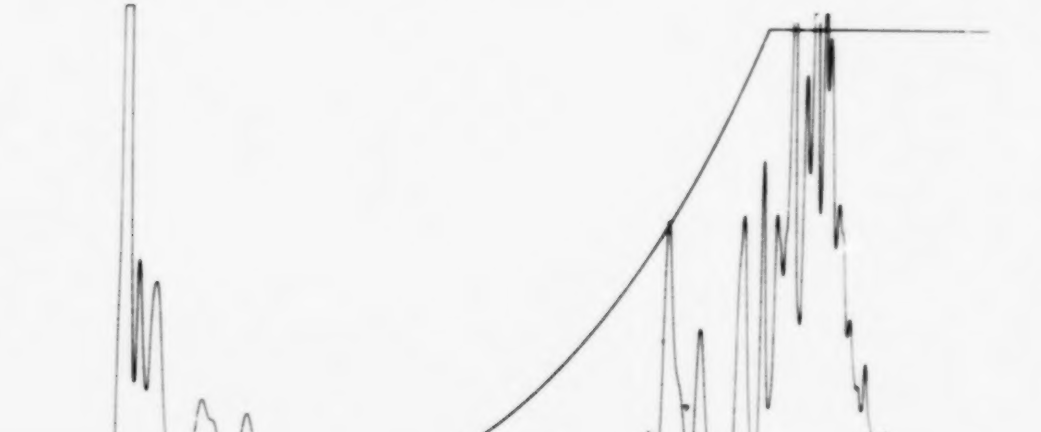


Figure 22. Survey liquid chromatogram of 100°-105°C organic layer from steam distillation.

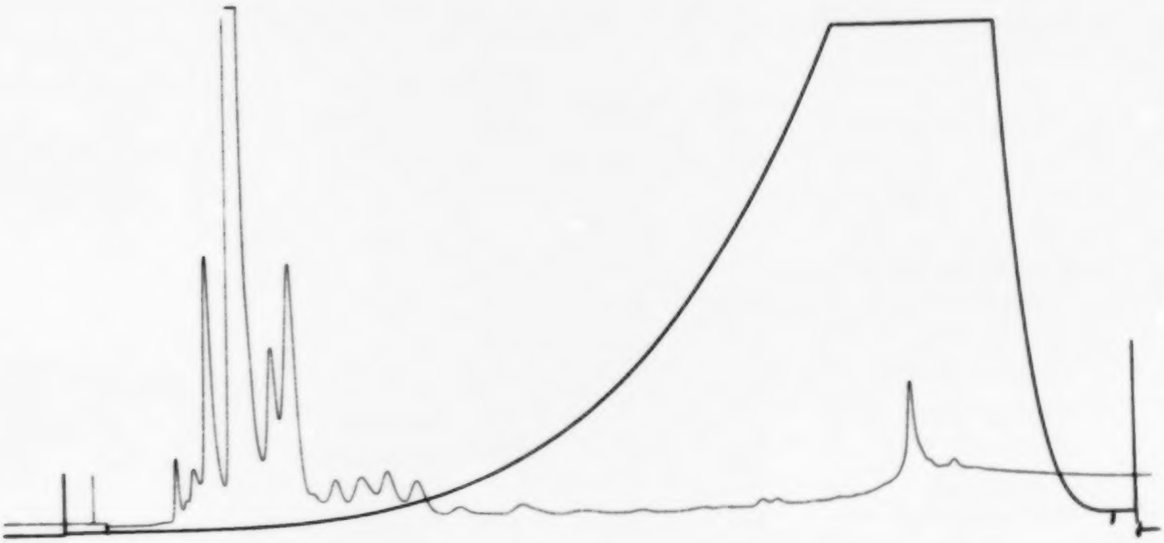


Figure 23. Survey liquid chromatogram of 100^{o}-$105^{o}C$ aqueous phase from steam distillation.

TABLE 6. HYDROGENATIONS AT MODERATE PRESSURE*

No.	Sample Source	Weight g	Water %	Weight "dry" oil†	Initial pressure, psig	Time hrs	H_2 Absorbed mg/g on "dry" basis
1	Coredle Condenser Oil	32.2	19.5	26.0	55.2	18	1.4
2	Blue IV Hardwood Composite Oil	20.8	12.8	18.1	55.5	20	4.9
3	Blue IV Pine Composite Oil	24.1	17.8	19.8	56.0	26	2.2
4	Blue IV Fan Hardwood Oil‡	65.1	12.4	57.0	Ambient pressure	60	1.1
5	Blue IV Fan Hardwood Oil	54.0	12.4	47.3	55.1	22	2.7
6	Blue IV Fan Hardwood Oil	52.1	12.4	45.6	55.3	72	1.9
7	Blue IV Fan Hardwood Oil	68.8	12.4	60.3	56.2	72	1.4
8	Blue IV Fan Pine Oil	45.9	17.9	37.7	57.2	24	2.4
9	Blue IV Fan Pine Oil	56.9	17.9	46.7	57.1	24	2.4
10	Blue IV Fan Pine Oil, Vacuum Stripped	34.4	0	34.4	58.1	26	1.8
11	Blue IV Fan Hardwood Oil, Vacuum Stripped	59.0	0	59.0	59.0	60	2.8

* 5% Pd on activated carbon was used in all experiments except 6 and 7, in which 5% Pt on activated carbon was used. Two grams of catalyst were used in each experiment. Approximately 200 ml of absolute ethanol was used for each hydrogenation.

† Calculated dry weight of oil based on percent water.

‡ This experiment was conducted in the recycle apparatus at ambient pressure.

TABLE 7. HYDROGENATIONS AT INTERMEDIATE PRESSURE

No.	Sample Source	Initial Pressure Atmospheres	H_2 Absorbed mg/g
12	Blue IV Fan Pine Oil	18.0	2.1
13	Blue IV Fan Pine Oil	19.5	2.1
14	Blue IV Fan Pine Oil	20.0	2.1

EXPERIMENTAL--PHASE II

SEPARATION EXPERIMENTS

The objective of this phase on separation work with pyrolytic oils was to obtain preliminary data on some approaches that could possibly be used for development of a process that would produce more refined fractions of oil that contain predominantly one chemical class of compounds. The broad classes of chemical substances in raw pyrolysis oil are phenolics, aromatic neutral compounds (neutrals of high aromaticity, NHA), acidic compounds, and a group of substances with "sugar-type" characteristics which are termed polyhydroxy neutral compounds (PNC). The emphasis in the separation experiments has been, therefore, to focus on obtaining fractions of the oil that contain essentially one of the general classes of substances in the oils. This is a report of the laboratory work of this phase at the bench level on a batch basis.

The five major approaches involving extraction techniques that were tested are:

A - Extraction of oil sequentially with water at 25°C, 50°C, and 95°C.

B - Extraction of oil with sodium sulfate solution (salting-out effect).

C - Extraction of oil simultaneously with an organic solvent and water (three phase system).

D - Extraction of sodium hydroxide soluble fractions of pyrolysis oil.

E - Extraction of organic solvent solutions of pyrolysis oil with water.

Vacuum Stripping of Raw Oil

Based on a number of extraction and separation experiments on a batch basis with raw and vacuum stripped pyrolysis oils, vaouum stripped oil gave better results than the raw oils. The vacuum stripping provides for the removal of the volatile organics and most of the water in the oil with potential subsequent recovery of these organic compounds. Our analysis show that the major organic component in the volatile fraction is acetic acid. For these reasons, our preliminary separation techniques are based on using vacuum stripped oil. Figure 24 shows schematically the vacuum stripping of the oil with yields.

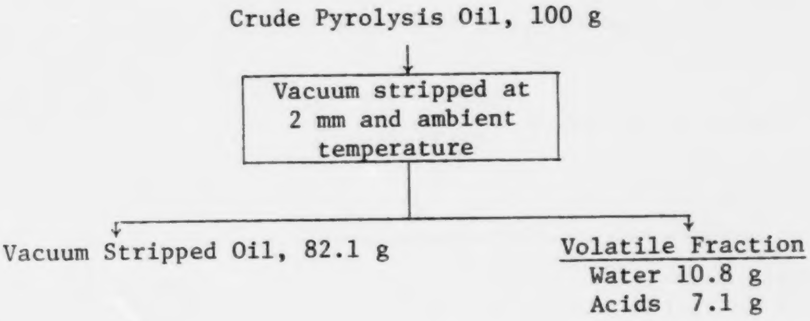

Crude Pyrolysis Oil, 100 g
Vacuum stripped at 2 mm and ambient temperature
Vacuum Stripped Oil, 82.1 g
Volatile Fraction
Water 10.8 g
Acids 7.1 g

Figure 24. Removal of volatiles from pyrolytic oil.

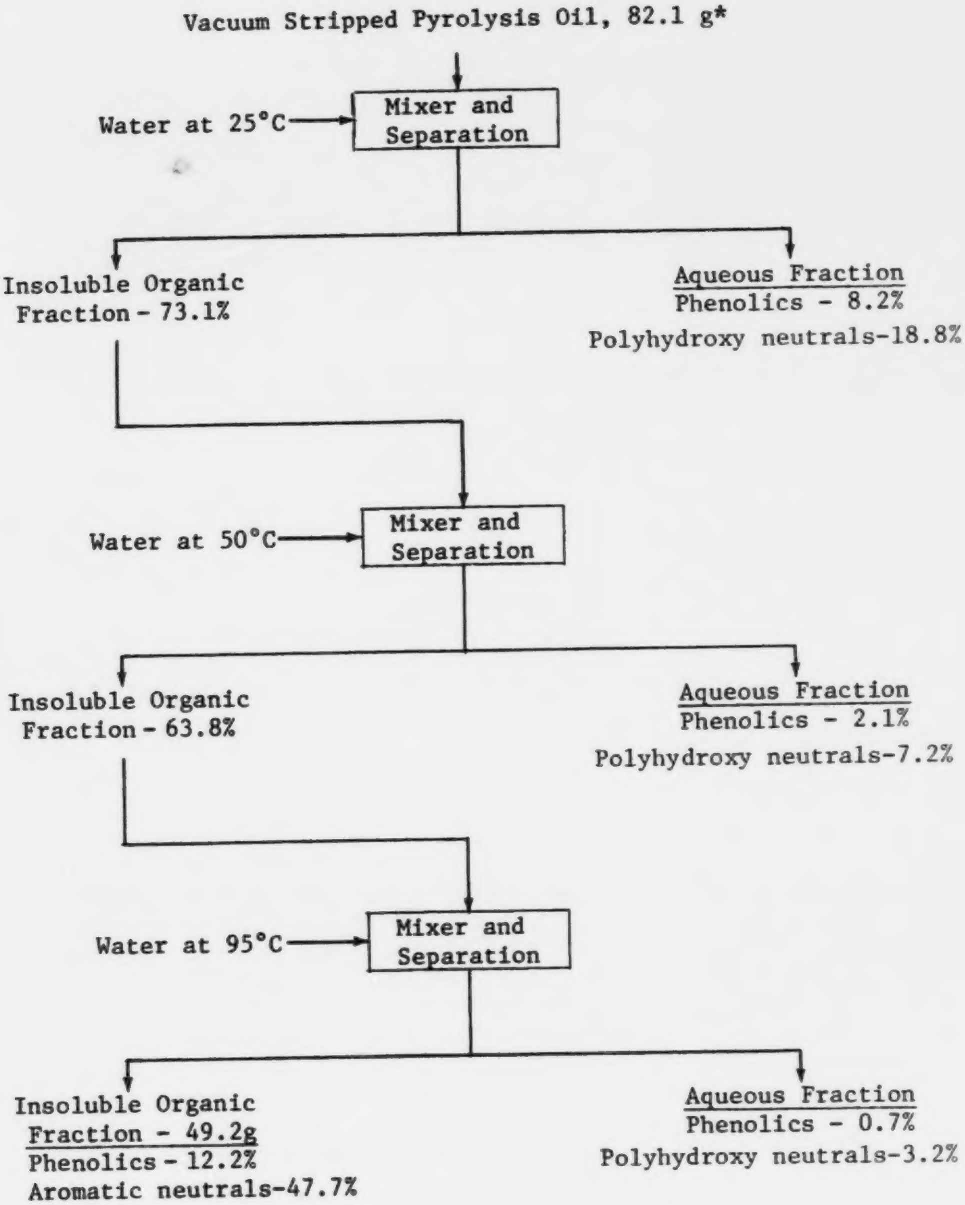
Extraction of Oil Sequentially with Water at 25°C, 50°C, and 95°C

A sample of vacuum stripped oil was extracted sequentially with water at 25°C, 50°C and 95°C in an effort to separate the more water soluble substances. Figure 25 shows schematically this separation process and the recovery of the different fractions are given in TABLE 8. The overall recovery was good. The liquid chromatogram, Figure 26, shows that the water extract is essentially free of the components of the oil which emerge in the latter two-thirds of the liquid chromatogram of the raw oil, Figure 15. The liquid chromatogram, Figure 27, shows that most of the components that appear in the initial part of the liquid chromatogram of the raw oil has been extracted sequentially with water at 25°C, 50°C, and 95°C. The liquid chromatograms of the water extract fractions at 50°C and 95°C were very similar to Figure 26 of the 25°C water extract.

The significance of these results is that the oil can be separated into water soluble and water insoluble fractions which offer the opportunity for recovery of useful fractions of aromatic compounds. The water insoluble fractions, based on our analysis, are composed of phenolics and neutral aromatics. The separation of this fraction into a highly concentrated phenolic fraction and highly concentrated fraction of aromatic neutral compounds could probably be accomplished by either fractional distillation or extraction with alkaline solution. The aqueous phases could be combined and subjected to a separation of the components with an aqueous salt solution as described below to yield a fraction with mainly phenolics and another fraction with mainly polyhydroxy neutral substances.

Extraction of Oil with Sodium Sulfate Solution

An extraction experiment with a sodium sulfate solution (90% saturated) was conducted to determine if extraction with aqueous salt solutions would offer a useful separation of the oil. The schematic for this extraction is shown in Figure 28, and the overall recovery was good.


Vacuum Stripped Pyrolysis Oil, 82.1 g*
Water at 25°C
Mixer and Separation
Insoluble Organic Fraction - 73.1%
Aqueous Fraction
Phenolics - 8.2%
Polyhydroxy neutrals-18.8%
Water at 50°C
Mixer and Separation
Insoluble Organic Fraction - 63.8%
Aqueous Fraction
Phenolics - 2.1%
Polyhydroxy neutrals-7.2%
Water at 95°C
Mixer and Separation
Insoluble Organic Fraction - 49.2g
Phenolics - 12.2%
Aromatic neutrals-47.7%
Aqueous Fraction
Phenolics - 0.7%
Polyhydroxy neutrals-3.2%

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*82.1g of vacuum stripped oil was obtained from 100g of this raw oil.

Figure 25. Extraction of oil sequentially with water at 25°C, 50°C, and 95°C.

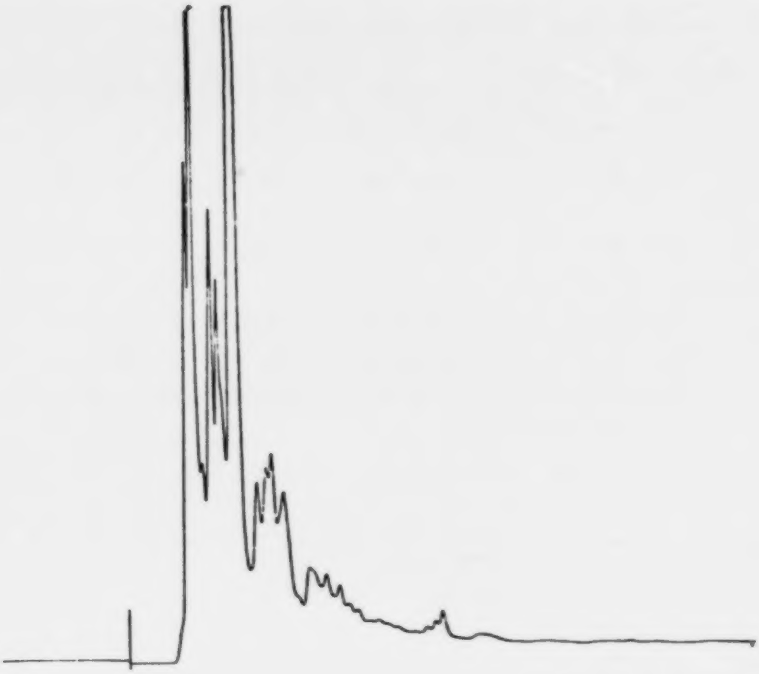


Figure 26. Liquid chromatogram of 25°C water extract of pyrolytic oil.

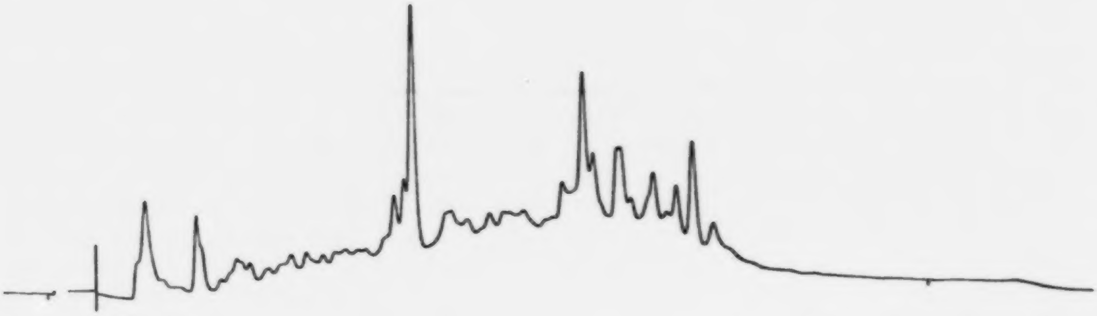


Figure 27. Liquid chromatogram of pyrolytic oil after successive extraction with water at 25°C, 50°C, and 95°C.

TABLE 8. YIELDS OF FRACTIONS FROM WATER EXTRACTION OF OIL

	Water Insoluble Fraction	Water Soluble Fractions			
		25°	50°	95°	Total
Phenolics	10 g	6.7 g	1.7 g	0.6 g	9.0 g
Aromatic neutrals	39.2 g	--	--	--	--
Polyhydroxy neutrals	--	15.4 g	5.9 g	2.6 g	23.9 g
Totals	49.2 g	22.1 g	7.6 g	3.2 g	32.9 g

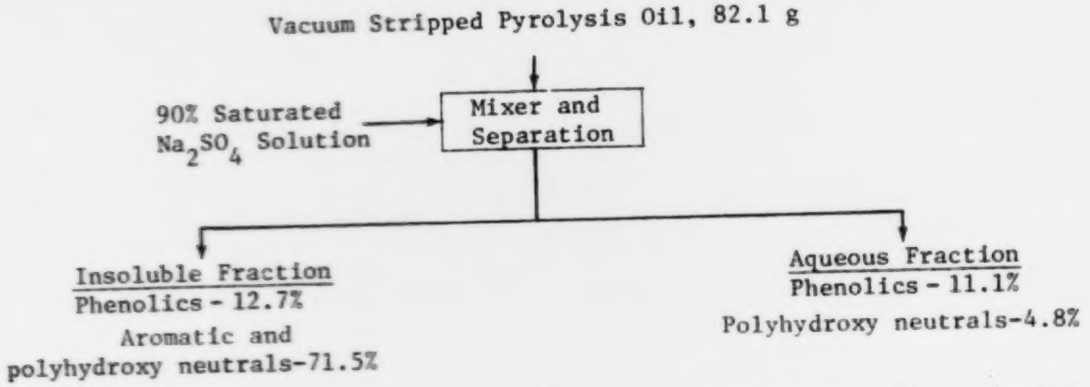

Vacuum Stripped Pyrolysis Oil, 82.1 g
90% Saturated Na_2SO_4 Solution
Mixer and Separation
Insoluble Fraction
Phenolics - 12.7%
Aromatic and polyhydroxy neutrals-71.5%
Aqueous Fraction
Phenolics - 11.1%
Polyhydroxy neutrals-4.8%

Figure 28. Extraction of pyrolytic oil with sodium sulfate solution.

The importance of these results is that with the sodium sulfate solution approximately 82% of the polyhydroxy neutrals are in the insoluble fraction with about 18% in the aqueous fraction. The phenolics are approximately 70% of the organics in this aqueous fraction. There are two approaches that can be used involving the sodium sulfate extraction. One approach would be to use the sodium sulfate extraction as the first step as shown in Figure 28 to produce an aqueous fraction of mainly phenolics. The insoluble organic fraction would then be treated with water extraction as depicted in Figure 25 to remove the polyhydroxy neutrals. The other approach would be to treat the oil as outlined in Figure 25, and then the three aqueous fractions would be combined followed by the addition of sodium sulfate. This approach could possibly provide a good separation between the phenolics and the polyhydroxy neutrals. The addition of a water insoluble organic solvent may be necessary in such a step to serve as a solvent for the polyhydroxy neutrals.

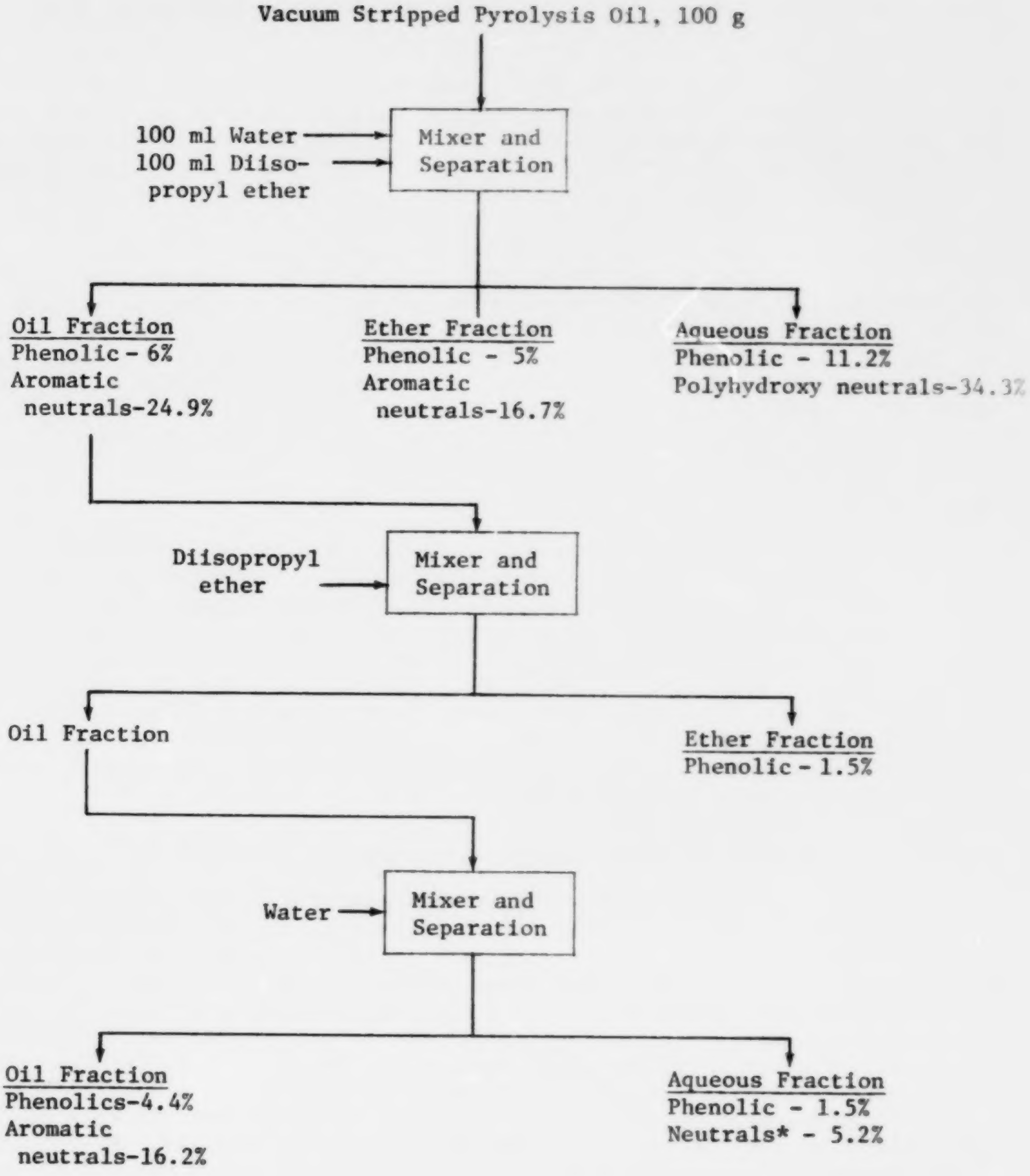
Extraction of Oil Simultaneously with Organic Solvents and Water: Three Phase System

Organic solvents offer a good potential for effecting separation of pyrolysis oils into fractions which contain very similar organic compounds. Some extractions with diisopropyl ether and anisole (methylphenyl ether) were tried with vacuum stripped oil. It was found difficult to have good contact of the organic solvent with only the oil because of the increase in the viscosity of the oil. Addition of an equal volume of water to the mixture produced a nonviscous three-phase-system containing an ether phase, an aqueous phase and a heavy oil phase with an overall recovery of approximately 96%. The schematic for diisopropyl ether and water separation along with yields is shown in Figure 29 and the schematic for anisole and water, Figure 30. Based on our analysis, the phenolics in the water fraction are mainly dihydroxy phenols; in the diisopropyl ether phase, alkylphenols; and in oil phase, ether phenols. The aqueous phases from both of the diisopropyl ether-water separations could be combined and possibly separated into a highly concentrated phenolic fraction by salting out the polyhydroxy neutrals with addition of sodium sulfate or some other salt.

In the anisole experiment, the phenolics were evenly divided between the anisole fraction and the aqueous fraction with a small amount in an oil insoluble fraction. About 88% of the aromatic neutrals were extracted into the anisole fraction, which contained about 62% of the original charge. A good potential step for processing this fraction would be fractional distillation. The oil insoluble fraction, which contained about 8.4% of the original charge, was approximately 85% aromatic neutrals and could be further processed by fractional distillation. The aqueous phase could be treated by the salting out technique with sodium sulfate as shown in Figure 27 to yield a highly concentrated phenolic fraction.

Extraction of Sodium Hydroxide Soluble Fractions of Pyrolysis Oil

A sample of vacuum stripped pyrolysis oil (154 g) was treated with 300 ml of 2% sodium hydroxide solution and approximately 52.6% dissolved. A series of methylene chloride extractions then were made at three different pH ranges. The "insoluble oil phase" upon treatment with additional 2% sodium hydroxide solution, dissolved in 400 ml of the alkaline solution. This solution was subjected to a series of methylene chloride extractions at the same pH ranges. The schematic for these extractions were presented in Figure 31. The overall recoveries were good, and the yield data are presented in TABLE 9. An examination of the data shows that phenolics are obtained with methylene chloride at each pH range and approximately 52% of the phenolics remain in the aqueous phase at pH range 1 to 3. The significance of this experiment is that the pyrolysis oil will dissolve in sufficient sodium hydroxide solution which offers the opportunity for a series of extractions at different pH ranges and also with a variety of organic solvents.


Vacuum Stripped Pyrolysis Oil, 100 g
100 ml Water
100 ml Diisopropyl ether
Mixer and Separation
Oil Fraction
Phenolic - 6%
Aromatic neutrals-24.9%
Ether Fraction
Phenolic - 5%
Aromatic neutrals-16.7%
Aqueous Fraction
Phenolic - 11.2%
Polyhydroxy neutrals-34.3%
Diisopropyl ether
Mixer and Separation
Oil Fraction
Ether Fraction
Phenolic - 1.5%
Water
Mixer and Separation
Oil Fraction
Phenolics-4.4%
Aromatic neutrals-16.2%
Aqueous Fraction
Phenolic - 1.5%
Neutrals* - 5.2%

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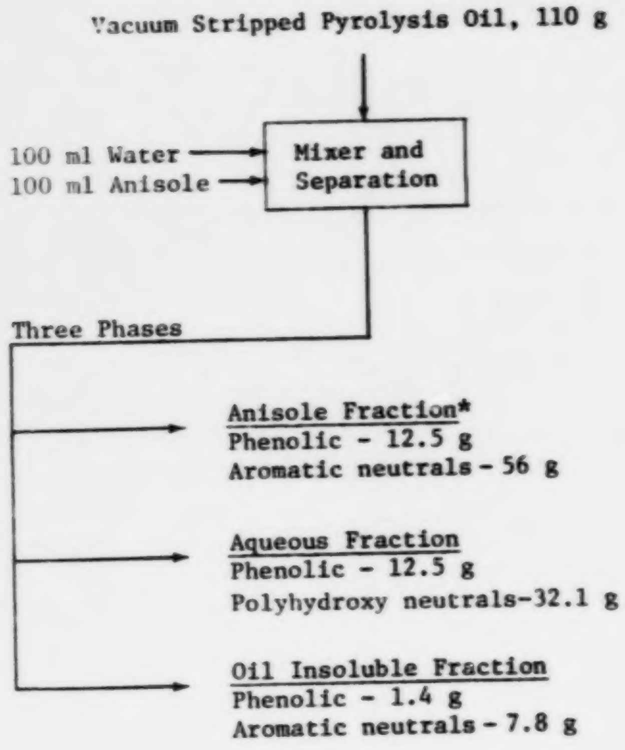
*Chemical nature unknown.

Figure 29. Combined diisopropyl and water extraction of pyrolytic oil.


Vacuum Stripped Pyrolysis Oil, 110 g
100 ml Water
100 ml Anisole
Mixer and Separation
Three Phases
Anisole Fraction*
Phenolic - 12.5 g
Aromatic neutrals - 56 g
Aqueous Fraction
Phenolic - 12.5 g
Polyhydroxy neutrals-32.1 g
Oil Insoluble Fraction
Phenolic - 1.4 g
Aromatic neutrals - 7.8 g

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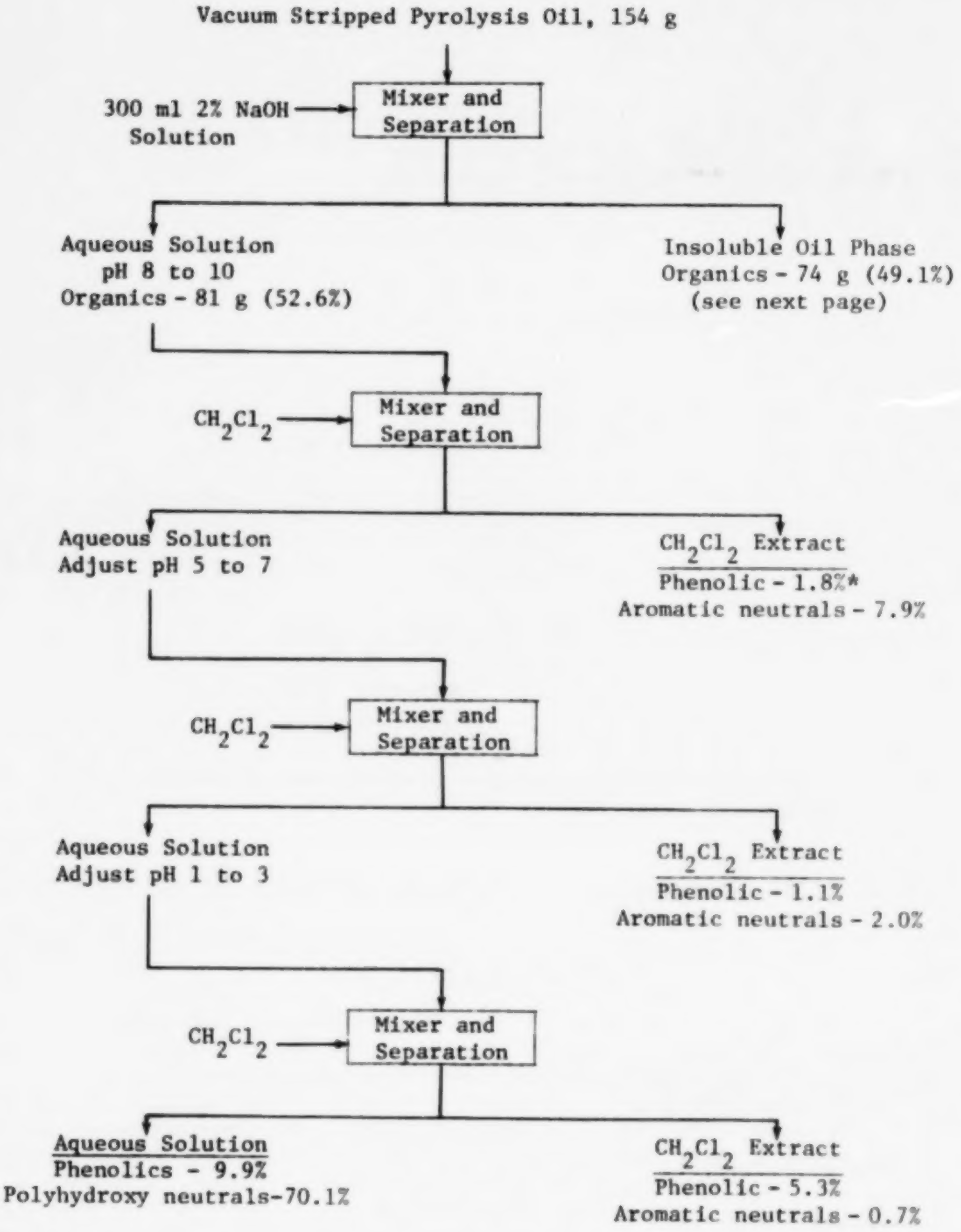
*The removal of all anisole from this fraction was difficult so that total recovery is greater than 100%.

Figure 30. Combined anisole and water extraction of pyrolytic oil.

Extraction of Organic Solvent Solutions of Oil

The vacuum stripped pyrolysis oil dissolves in methylene chloride and in n-butanol to give complete solutions. Solutions of vacuum stripped oil in methylene chloride were extracted with water and the combined water extracts were then extracted in one experiment with diisopropyl ether and in a second experiment with methyl isobutyl ketone (MIBK). The schematics for these two experiments are shown in Figures 32 and 33. The data are summarized in TABLE 10. The significance of the data in these experiments is that a fraction of phenolics is obtained with MIBK which contains less than 10% other organics. An examination of the data will also indicate one of the difficulties encountered in working with pyrolysis oils. One would expect the quantity of phenolics in the final methylene chloride fractions to be in closer agreement. The lack of agreement can be attributed to differences in experimental techniques and to the need of improvement in analytical techniques.


Vacuum Stripped Pyrolysis Oil, 154 g
300 ml 2% NaOH Solution
Mixer and Separation
Aqueous Solution pH 8 to 10 Organics - 81 g (52.6%)
Insoluble Oil Phase Organics - 74 g (49.1%) (see next page)
CH_2Cl_2
Mixer and Separation
Aqueous Solution Adjust pH 5 to 7
CH_2Cl_2 Extract
Phenolic - 1.8%*
Aromatic neutrals - 7.9%
CH_2Cl_2
Mixer and Separation
Aqueous Solution Adjust pH 1 to 3
CH_2Cl_2 Extract
Phenolic - 1.1%
Aromatic neutrals - 2.0%
CH_2Cl_2
Mixer and Separation
Aqueous Solution
Phenolics - 9.9%
Polyhydroxy neutrals-70.1%
CH_2Cl_2 Extract
Phenolic - 5.3%
Aromatic neutrals - 0.7%

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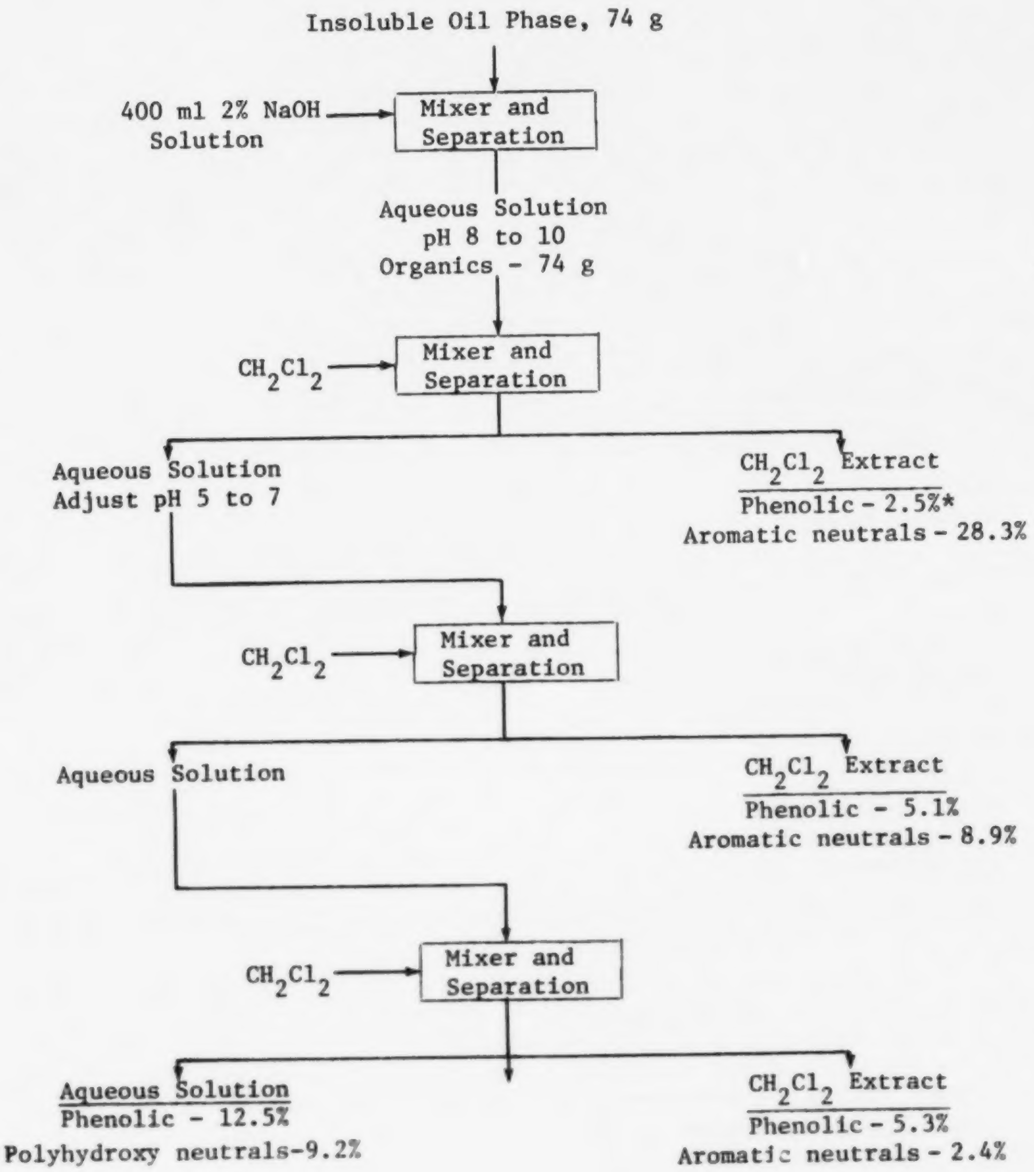
*Percent yield is based on weight of material extracted from 81 g of organics.

Figure 31. Extraction of pyrolytic oil with 2% sodium hydroxide solution.

Vacuum Stripped Pyrolysis Oil, 154 g (cont'd)


Insoluble Oil Phase, 74 g
400 ml 2% NaOH Solution
Mixer and Separation
Aqueous Solution pH 8 to 10 Organics - 74 g
CH_2Cl_2
Mixer and Separation
Aqueous Solution Adjust pH 5 to 7
CH_2Cl_2 Extract
Phenolic - 2.5%*
Aromatic neutrals - 28.3%
CH_2Cl_2
Mixer and Separation
Aqueous Solution
CH_2Cl_2 Extract
Phenolic - 5.1%
Aromatic neutrals - 8.9%
CH_2Cl_2
Mixer and Separation
Aqueous Solution
Phenolic - 12.5%
Polyhydroxy neutrals-9.2%
CH_2Cl_2 Extract
Phenolic - 5.3%
Aromatic neutrals - 2.4%

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*Percent yield is based on weight of material extracted from 74 g organics.

Figure 31 (cont'd). Extraction of pyrolytic oil with 2% sodium hydroxide solution.

TABLE 9. YIELDS FROM METHYLENE CHLORIDE EXTRACTIONS OF ALKALINE SOLUTIONS OF PYROLYTIC OIL

Fraction	First Series CH_2Cl_2 Extractions Weighting	Second Series CH_2Cl_2 Extractions Weighting	Total Yield	% Yield
pH 8 to 10				
Phenolics	1.46	1.85	3.31	2.17
Aromatic neutrals	6.4	20.9	23.3	17.9
pH 5 to 7				
Phenolics	0.89	3.77	4.67	3.06
Aromatic neutrals	1.62	6.56	8.21	5.38
pH 1 to 3				
Phenolics	4.29	3.92	8.21	5.38
Aromatic neutrals	0.57	1.78	2.35	1.54
Aqueous Phase				
Phenolics	8.02	9.25	17.3	11.3
Polyhydroxy neutrals	56.8	6.81	63.6	41.7
Tar neutrals	-	17.5	17.5	11.8
Totals				
Phenolics	-	-	33.5	21.9
Aromatic neutrals	-	-	37.9	24.8
Polyhydroxy neutrals	-	-	63.9	41.7
Tar neutrals	-	-	17.5	11.8

The vacuum stripped pyrolysis oil is soluble in n-butanol, and an aqueous extraction experiment with a n-butanol solution of pyrolysis oil was carried out to determine the distribution of the phenolic and other organics between the aqueous and n-butanol fractions. The schematic for this experiment with yields for each fraction is given in Figure 34. The important result of this experiment is the reduced amount of polyhydroxy neutrals in the aqueous phase as compared with the other extractions with the exception of the sodium sulfate extraction. There is the potential that extraction of a n-butanol solution of pyrolysis oil with sodium sulfate solution could yield an aqueous solution with a high concentration of phenolics relative to other organics. In this experiment, material recovery is not too good because in the removal of the n-butanol at low vacuum, some of the more volatile aromatic compounds were lost.

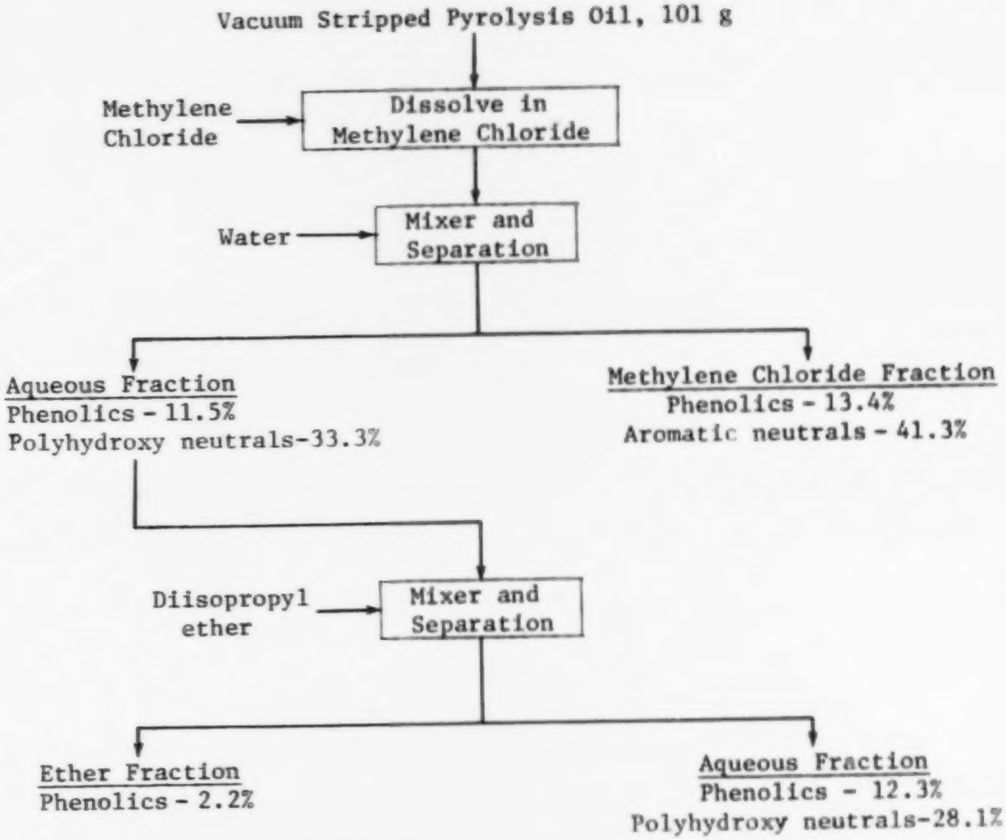

Vacuum Stripped Pyrolysis Oil, 101 g
Methylene Chloride
Dissolve in Methylene Chloride
Water
Mixer and Separation
Aqueous Fraction
Phenolics - 11.5%
Polyhydroxy neutrals-33.3%
Methylene Chloride Fraction
Phenolics - 13.4%
Aromatic neutrals - 41.3%
Diisopropyl ether
Mixer and Separation
Ether Fraction
Phenolics - 2.2%
Aqueous Fraction
Phenolics - 12.3%
Polyhydroxy neutrals-28.1%

Figure 32. Extraction of methylene chloride solution of pyrolytic oil with water followed by diisopropyl ether extraction of aqueous fraction.

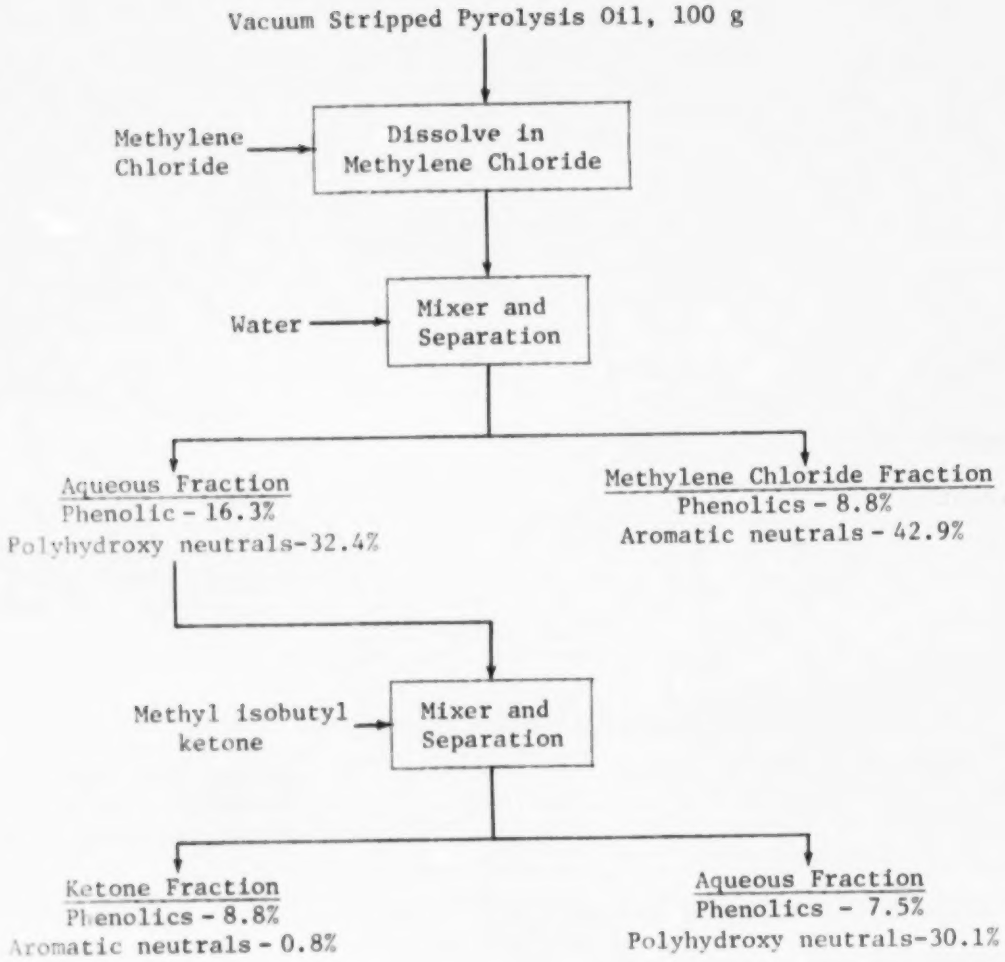

Vacuum Stripped Pyrolysis Oil, 100 g
Methylene Chloride
Dissolve in Methylene Chloride
Water
Mixer and Separation
Aqueous Fraction
Phenolic - 16.3%
Polyhydroxy neutrals-32.4%
Methylene Chloride Fraction
Phenolics - 8.8%
Aromatic neutrals - 42.9%
Methyl isobutyl ketone
Mixer and Separation
Ketone Fraction
Phenolics - 8.8%
Aromatic neutrals - 0.8%
Aqueous Fraction
Phenolics - 7.5%
Polyhydroxy neutrals-30.1%

Figure 33. Extraction of methylene chloride solution of pyrolytic oil with water followed by methylisobutyl ketone extraction of aqueous fraction.

TABLE 10. YIELDS IN FINAL FRACTIONS FROM SEPARATION TECHNIQUES IN FIGURES 32 AND 33

Final Fraction	Diisopropyl Ether Experiment	Methylisobutyl Ketone Experiment
Methylene chloride		
Phenolics	13.5 g	8.8 g
Aromatic neutrals	41.7 g	42.9 g
Aqueous		
Phenolics	12.4 g	7.5 g
Polyhydroxy neutrals	28.4 g	30.1 g
Organic solvent		
Phenolics	2.2 g	8.8 g
Aromatic neutrals	0	0.8 g

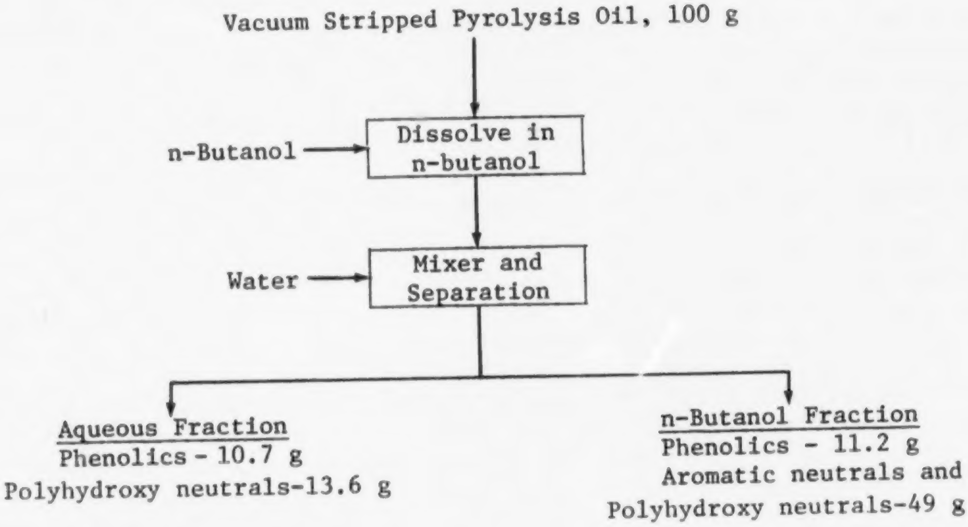

Vacuum Stripped Pyrolysis Oil, 100 g
n-Butanol
Dissolve in n-butanol
Water
Mixer and Separation
Aqueous Fraction
Phenolics - 10.7 g
Polyhydroxy neutrals-13.6 g
n-Butanol Fraction
Phenolics - 11.2 g
Aromatic neutrals and
Polyhydroxy neutrals-49 g

Figure 34. Extraction of n-butanol solution of pyrolytic oil with water.

EXPERIMENTAL--PHASE III

PYROLYTIC OIL

The pyrolytic oil for this experimental phase was taken from the oil produced in a run in the Georgia Tech pyrolysis pilot plant (capacity, 225 kg/hr) on October 12, 1978. The converter feedstock was pine chips dried to contain approximately six percent moisture, and the air-to-feed input ratio was continually adjusted within a narrow range to maintain a temperature of 125° to 130°C in the off-gases passing from the headspace of the reactor to the condensers. The condenser temperatures were held near 75°C. These closely controlled low temperatures resulted in less thermal cracking than had been observed in earlier converter runs with higher temperatures.

The selected containers of pyrolytic oil were stirred thoroughly and the moisture content of the oil in each container was determined. Two four-liter reference samples were taken from each container and stored in tightly capped plastic containers for future reference. The remaining oil was combined and thoroughly mixed. Eight four-liter samples were stored in tightly closed plastic containers for laboratory work. The remaining oil was stored in tightly closed plastic lined containers as a reserve supply.

Characterization of Pyrolytic Oil Sample

The percent moisture in the sample was determined by azeotropic distillation with toluene (Dean and Stark Method). The percent solid material, mainly fine fiber and char fines, was determined by dissolving a weighed portion of the oil in a large excess of acetone and passing the solution through a tared glass filter paper. The filter paper and residue were thoroughly washed with acetone, dried, and weighed. The percent ash was determined by charring weighed oil samples in tared crucibles by means of an infra-red lamp, igniting the char in a muffle furnace, and determining the weight of the ash. Sulfur was determined by igniting two-gram oil samples at 30 atmospheres in an oxygen bomb calorimeter. No turbidity was observed when barium chloride was added to filtered washings from the oxygen bomb, and no increase was observed in the weight of tared Gooch crucibles used to filter the solution of barium chloride in the washings. The density of the mixed oil sample was calculated from the weight of 200 ml at 25°C. The percent of carbon, hydrogen and nitrogen was determined using a Perkin Elmer Model 240 Elemental Analyzer. Results of these characterizations are shown in TABLE 11.

SEPARATION EXPERIMENTS

The results of the experimental work in Phase II with different extraction techniques with pyrolytic oil were carefully evaluated for further investigation for the development of a pilot plant concept for processing

TABLE 11. PROPERTIES OF PYROLYTIC OIL SAMPLE

Determined	Sample 1	Sample 2	Average
Percent Moisture	14.7	14.9	14.8
Percent Solids	0.38	0.43	0.41
Percent Ash	0.055	0.054	0.055
Percent Sulfur	<0.001	<0.001	<0.001
Percent Carbon	57.27	57.34	57.30
Percent Hydrogen	6.72	6.76	6.74
Percent Nitrogen	0.06	0.06	0.06
Density (g/mℓ)	1.234	1.234	1.234

pyrolytic oils. The selected processes were aqueous extraction (Process No. 1), simultaneous extraction with water and an organic solvent (Process No. 2), and dissolution of the pyrolytic oil in an organic solvent followed by aqueous extraction of the solution (Process No. 3). The first efforts were with batch experiments of all three processes in which both vacuum stripped and unstripped oil samples were examined and the effects of both polar and nonpolar solvents were studied. Based on the results of the batch experiments, Process No. 1 and Process No. 2 using a polar organic solvent were chosen for continuous countercurrent extractions of both vacuum stripped and unstripped pyrolytic oil. The batch experiments will be described first followed by the description of the continuous extraction experiments.

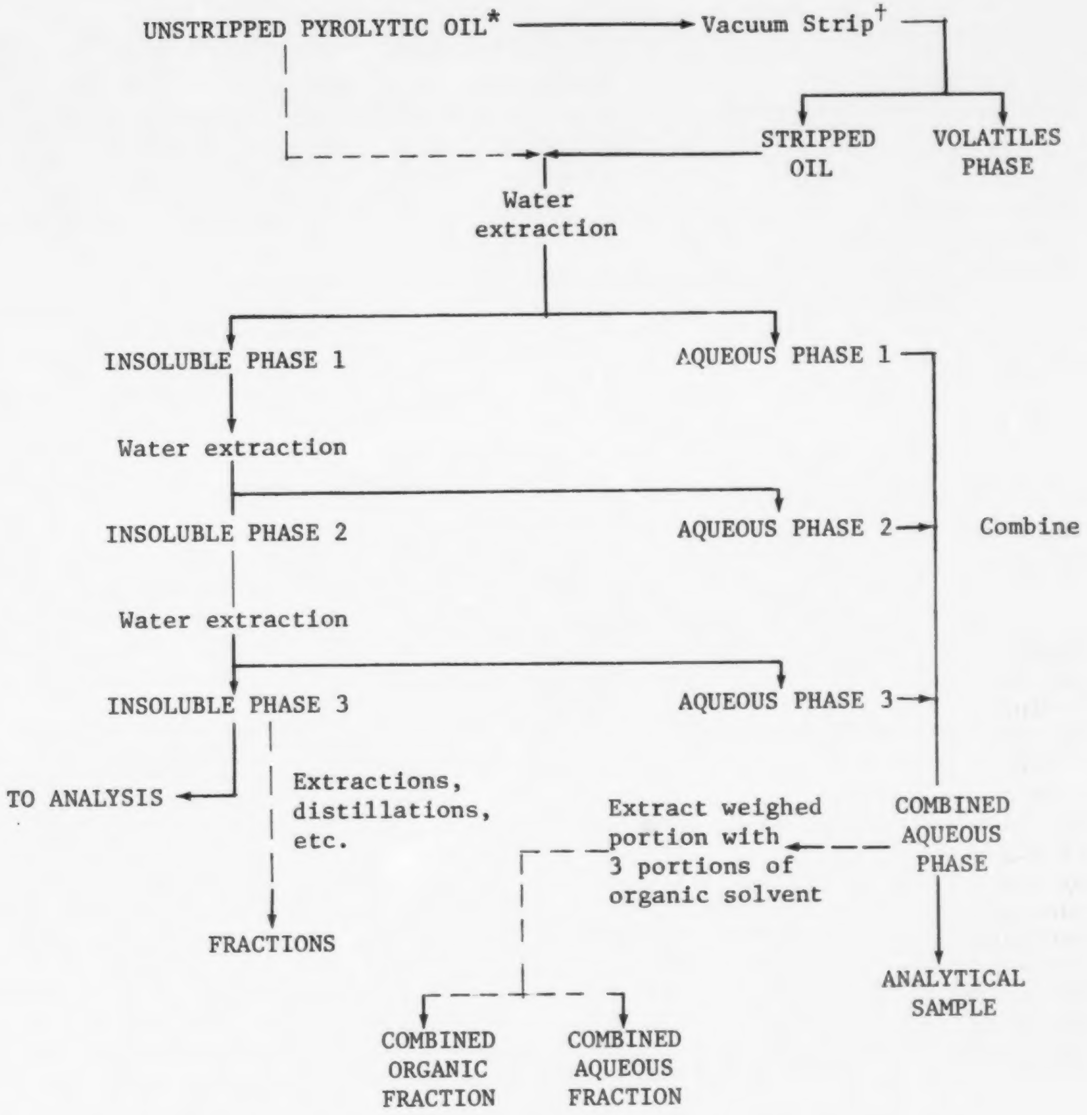
Initial Batch Separation Procedures

The batch separations were performed by stirring approximately 100, 200, or 500 g of oil, weighed to the nearest 0.1 g, with the extracting solvent system for 30 minutes in a tall form 1,000 ml beaker at approximately 900 revolutions per minute using a 4 cm PTFE coated bar with a magnetic stirrer. At the end of the contact period the beaker was chilled to immobilize the insoluble tar phase so that the extracting solvent phase or phases could be removed by decantation. Conventional separatory funnels were used to separate the aqueous and immiscible organic solvent phases.

Process No. 1. Water Extraction Procedures--

Six samples of pyrolytic oil were extracted with water, and the water phases were separated from the insoluble organic phases by decantation. Two additional aqueous extractions were made, each using the insoluble organic phase from the preceding extraction. A schematic flow diagram of this procedure is shown in Figure 35, which shows the treatment of unstripped pyrolytic oil by vacuum stripping and subsequent water extraction as solid lines at the top of the figure and by water extraction without vacuum stripping as a broken line at the top of the figure. The broken lines at the bottom of the figure indicate generalized further treatments of the separated phases.

Six samples of oil were extracted with water as listed below. The aqueous phase and insoluble organic phase from Extraction I (1) were used to


UNSTRIPPED PYROLYTIC OIL*
Vacuum Strip†
STRIPPED OIL
VOLATILES PHASE
Water extraction
INSOLUBLE PHASE 1
AQUEOUS PHASE 1
Water extraction
INSOLUBLE PHASE 2
AQUEOUS PHASE 2
Combine
Water extraction
INSOLUBLE PHASE 3
AQUEOUS PHASE 3
TO ANALYSIS
Extractions, distillations, etc.
FRACTIONS
Extract weighed portion with 3 portions of organic solvent
COMBINED AQUEOUS PHASE
ANALYTICAL SAMPLE
COMBINED ORGANIC FRACTION
COMBINED AQUEOUS FRACTION

---

*Samples and yields shown in UPPER CASE LETTERS

†Operations shown in lower case letters

Figure 35. Aqueous batch extraction, Process No. 1.

develop analytical techniques at Georgia Tech and at Atlanta University. The fractions from Extraction I (2-6) were used to experiment with techniques to obtain additional fractions. The separation techniques are described in a later section of this report.

- Extraction I (1)--A 102.9 g sample of vacuum stripped oil was extracted with three 100 ml portions of deionized water.
- Extraction I (2)--This experiment was a duplicate of I (1) to provide a water solution for subsequent extraction with a polar organic solvent.
- Extraction I (3)--This experiment was run as I (1) and I (2) to provide an aqueous solution for extraction with a nonpolar organic solvent.
- Extraction I (4)--This extraction was performed as I (1) except that a 203.4 g portion of unstripped oil was extracted with two 200 ml portions of water. The water extract was reserved for contact experiments with activated carbon.
- Extraction I (5)--This experiment was similar to I (4).
- Extraction I (6)--A 400 g unstripped oil sample was extracted with 400 ml water followed by two successive extractions with 200 ml portions of water.

The water solution fraction and water insoluble fraction were used for further analysis and testing of additional separation techniques.

No attempt was made to isolate individual compounds from the large number present in each separated phase or fraction. Quantitative analysis was directed only toward separating and identifying classes of compounds having similar solubilities or measurable chemical properties, which might be related to their potential commercial use. Based on analytical methods, which will be described in a later section of this report, the vacuum stripping and extraction yields were determined as volatile organics, nonvolatile organics (NVO), phenolics, polyhydroxy neutral compounds (PNC) and neutrals of high aromaticity (NHA). The polyhydroxy neutral compounds were estimated by subtracting the phenolics in the water phases or fractions from the corresponding total nonvolatile organics. Neutrals of high aromaticity were estimated by subtracting the phenolics from the total organics in an organic solvent phase or fraction. The results of the batch extraction, expressed as percent of the moisture-free unstripped oil sample, are shown in TABLE 12. Since the moisture free oil contained seven percent volatile compounds the total nonvolatile organics should approach 93 percent.

The percent nonvolatile organics (NVO) was determined by removing the solvent from a weighed sample of the separated phase on a rotary vacuum evaporator with caution to avoid heating. It is believed that incomplete solvent removal from the organic phase led to the apparently high total NVO values in Extractions I (2) and I (6). The aqueous phase from Extraction I (2) was extracted with three successive portions of methylisobutyl ketone (MIBK). The MIBK extracts were combined to form the MIBK fraction. The distributions of the classes of organic compounds in the MIBK fraction and the extracted water fraction are shown in parentheses. The distributions resulting from a similar extraction of the water phase in Experiment I (3) with chloroform are represented in a similar manner. The percent NVO was determined separately for each of the four successive water phases in Extraction I (6) to show the quantity of organic material removed by each extraction step. Since most of the water soluble material was found in the

TABLE 12. COMPOSITION OF YIELDS FROM BATCH WATER EXTRACTIONS, PROCESS NO. 1

Extraction Experiment	Percent NVO*	Percent Phenolic	Percent PNC†	Percent NHA‡
Extraction I (1)				
Aqueous Phase	53.8	28.7	25.1	-
Insoluble Organic Phase	39.8	13.7	-	26.1
Extraction I (2)				
Aqueous Phase	50.4	34.0	14.5	1.9
Aqueous Fraction	(38.5)	(24.0)	(14.5)	-
MIBK Fraction	(11.9)	(10.0)	-	(1.9)
Insoluble Organic Phase	55.5	5.5	-	50.0
Extraction I (3)				
Aqueous Phase	52.8	41.4	12.2	2.9
Aqueous Fraction	(41.7)	(33.2)	(12.2)	-
Chloroform Fraction	(11.1)	(8.2)	-	(2.9)
Insoluble Organic Phase	39.9	23.3	-	15.6
Extraction I (4)				
Aqueous Phase	40.1	Not Determined [Stock I(4)A]		
Insoluble Organic Phase	51.4	Not Determined [Stock I(4)0]		
Extraction I (5)				
Aqueous Phase	52.3	Not Determined [Stock I(5)A]		
Insoluble Organic Phase	41.4	Not Determined [Stock I(5)0]		
Extraction I (6)				
First Aqueous Phase, I(6)A1	44.6	13.6	31.0	-
Second Aqueous Phase, I(6)A2	6.0	Not Determined		
Third Aqueous Phase, I(6)A3	2.5	Not Determined		
Fourth Aqueous Phase, I(6)4	0.1	Not Determined		
Insoluble Organic Phase, I(6)0	55.8	11.9	-	43.9

* Non Volatile Organics

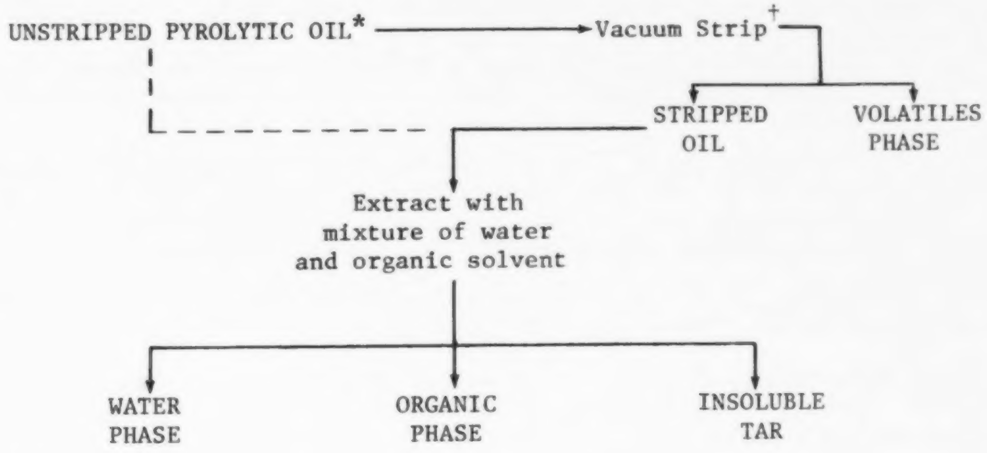
† Polyhydroxy Neutral Compounds

‡ Neutrals of High Aromaticity

first water phase, I(6) A1, only this phase was analyzed and reserved for further experiments.

Process No. 2. Three Phase Extraction Procedure--

In the three phase extraction technique the oil sample was extracted with a vigorously stirred mixture of water and an immiscible solvent. The liquid phases were decanted from the insoluble tar phase and separated into aqueous and organic phases. A schematic diagram of this process is shown in Figure 36.


UNSTRIPPED PYROLYTIC OIL*
Vacuum Strip†
STRIPPED OIL
VOLATILES PHASE
Extract with mixture of water and organic solvent
WATER PHASE
ORGANIC PHASE
INSOLUBLE TAR

---

* Samples and yields shown in UPPER CASE LETTERS

† Operations shown in lower case letters

Figure 36. Three phase extraction, Process No. 2.

Four batch extractions were performed using mixtures of water with MIBK as a polar organic solvent or water with chloroform as a nonpolar solvent as follows.

- Extraction II (1)--A 103.1 g sample of vacuum stripped oil was stirred with a mixture of 100 ml water and 100 ml MIBK. The mixture was allowed to stand, and the water and organic phases were separated.
- Extraction II (2)--Extraction II (2) was performed as II (1) using 105.6 g unstripped oil, 200 ml chloroform, and 100 ml water.
- Extraction II (3)--This extraction was similar to II (1) except that the sample was 97.9 g unstripped oil.
- Extraction II (4)--This experiment was run in the same manner as II (1).

The distributions of the main classes of compounds were determined following the scheme described above for Process No. 1. These distributions are shown in TABLE 13. The letter codes, e.g., II(1)A, shown after each phase are included to facilitate their identification as starting materials for additional experiments to be described in later sections of this report.

Process No. 3. Dissolution in an Organic Solvent Followed by Water Extraction--

In these experiments listed below, the oil sample was dissolved in an organic solvent, and the resulting solution was extracted with water. A schematic diagram of this process is shown in Figure 37.

- Extraction III (1)--A 102.6 g sample of vacuum stripped oil was stirred with 200 ml chloroform. The chloroform solution was extracted with three 100 ml portions of water.
- Extraction III (2)--This experiment was similar to III (1) except that 200 ml MIBK was used to dissolve the oil, and the three water extractions were carried out with a weighed fraction of the MIBK solution with proportionally smaller quantities of water.
- Extraction III (3)--This experiment was similar to III (2) except that the sample was unstripped oil.

The distributions of the identifiable classes of compounds were determined. These distributions are shown in TABLE 14. The chloroform insoluble material in Extraction III (1) was readily soluble in acetone or five percent aqueous alkali, which indicates that the neutral material in the insoluble tar phase contained a large number of hydroxyl groups. This interpretation was supported by infra-red examination. The MIBK insoluble tars in Extractions III (2) and III (3) were readily soluble in acetone but only partially dissolved in five percent aqueous alkali. With the support of infra-red evidence it was concluded that these MIBK insoluble tars were a mixture of polyhydroxy compounds and neutrals of high aromaticity.

Continuous Countercurrent Extraction Procedures

Results of the batch extraction experiments indicated that continuous countercurrent extraction work should be concentrated on Process No. 1 with subsequent extraction of the resulting solution phase with MIBK and on Process No. 2 using water and MIBK. Four experimental runs were made using Process No. 1 with vacuum stripped oil, Process No. 1 with unstripped oil, Process No. 2 with vacuum stripped oil and Process No. 2 with unstripped oil.

Modular construction was chosen for the countercurrent extractor to permit relocation of the inlet and outlet points and to permit variations in the length of the unstirred phase separation zones. A schematic diagram of the counter current extractor is shown in Figure 38.

The apparatus consisted of a vertical tube with a heavy tar outlet at the bottom and side inlets for solvent admission and a recycling line outlet in the lower sections of the tube. The diameter of the mixing chamber was larger than that of the settling zones to prolong the residence time of

TABLE 13. COMPOSITION OF YIELDS FROM BATCH THREE PHASE EXTRACTIONS, PROCESS NO. 2

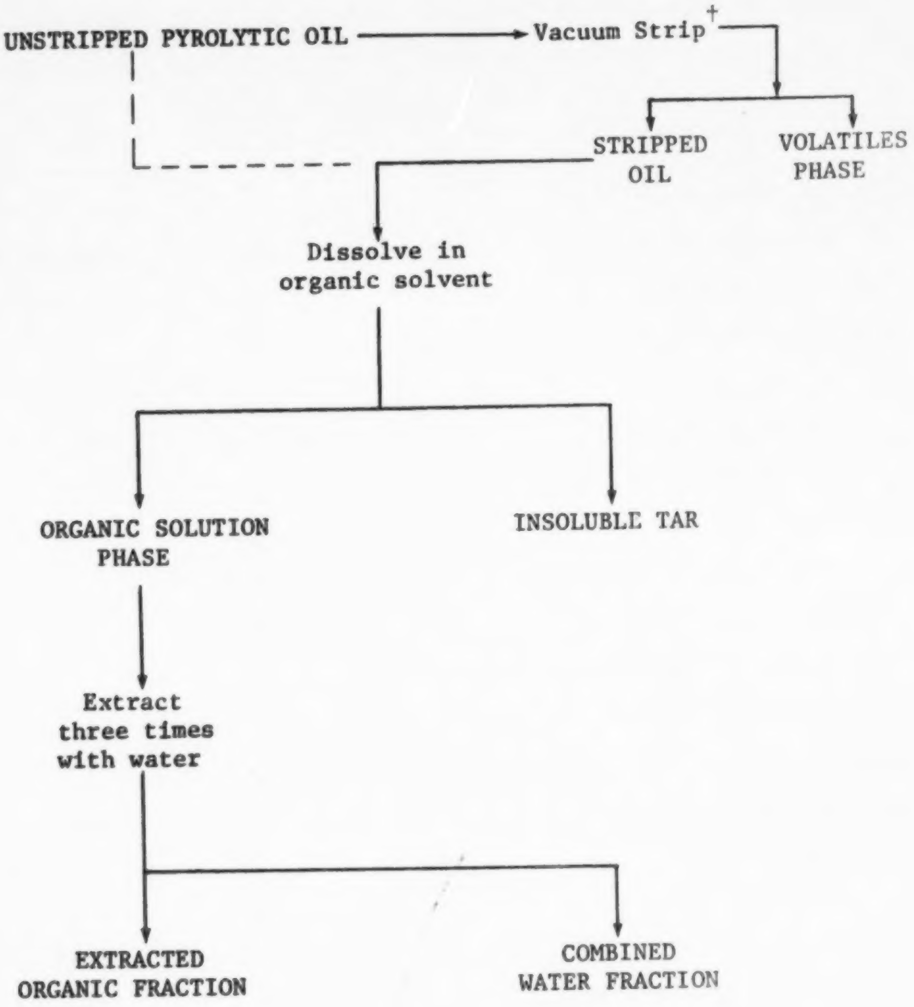
Extraction Experiment	Percent NVO*	Percent Phenolic	Percent PNC†	Percent NHA**
Extraction II (1)				
Aqueous Phase II(1)A	39.2	16.9	22.3	-
MIBK Phase II(1)M	53.0	22.1	-	30.9
Insoluble Tar Phase	0.1	ND‡		
Extraction II(2)				
Aqueous Phase II(2)A	41.0	17.9	23.1	-
Chloroform Phase II(2)C	51.7	21.3	-	30.4
Insoluble Tar Phase	2.2	ND		
Extraction II(3)				
Aqueous Phase II(3)A	38.7	ND		
MIBK Phase II(3)M	50.7	ND		
Insoluble Tar Phase	2.1			
Extraction II(4)				
Aqueous Phase II(4)A	41.6	7.9	33.7	-
MIBK Phase II(4)M	54.1	27.6	-	26.5
Insoluble Tar Phase	0.5	ND		

*Non volatile hydrocarbons

†Polyhydroxy neutral compounds

**Neutrals of high aromaticity

‡Not determined


UNSTRIPPED PYROLYTIC OIL
Vacuum Strip†
STRIPPED OIL
VOLATILES PHASE
Dissolve in organic solvent
ORGANIC SOLUTION PHASE
INSOLUBLE TAR
Extract three times with water
EXTRACTED ORGANIC FRACTION
COMBINED WATER FRACTION

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[*] Samples and yields shown in UPPER CASE LETTERS.

[†] Operations shown in lower case letters.

Figure 37. Sequential organic water extraction, Process No. 3.

TABLE 14. COMPOSITION OF YIELDS, PROCESS NO. 3

Extraction Experiments	Percent NVO*	Percent Phenolics	Percent PNC†	Percent NHA**
Extraction III(1)				
Chloroform Phase III(1)C	85.7	20.3	----- 65.4 -----	
First Aqueous Fraction III(1)A1	(27.5)	(12.8)	(14.7)	-
Second Aqueous Fraction III(1)A2	(3.5)	(2.5)	(1.0)	-
Third Aqueous Fraction III(1)A3	(1.4)	(0.8)	(0.6)	-
Extracted Chloroform Fraction III(1)CE	(36.6)	(6.4)	-	(30.2)
Insoluble Tar Phase III(1)MR	7.8	4.5	3.3	-
Extraction III(2)				
MIBK Phase III(2)M	77.1	23.4	----- 53.7 -----	
First Aqueous Fraction III(2)A1	(23.1)	(12.0)	(11.1)	-
Second Aqueous Fraction III(2)A2	(4.9)	(4.9)	(0)	-
Third Aqueous Fraction III(2)A3	(4.9)	(0.5)	(0)	-
Extracted MIBK Fraction III(2)ME	(44.2)	(6.5)	-	(37.7)
Insoluble Tar Phase III(2)MR	15.3	3.7	----- 11.6 -----	
Extraction III(3)				
MIBK Phase	65.1	26.8	----- 38.3 -----	
First Aqueous Fraction III(3)A1	(17.9)	(9.7)	(8.2)	-
Second Aqueous Fraction III(3)A2	(3.9)	(3.9)	(0)	-
Third Aqueous Fraction III(3)A3	(1.6)	(1.4)	(0.2)	-
Extracted MIBK Fraction III(3)ME	(41.1)	(7.6)	-	(33.5)
Insoluble Tar Phase III(3)MR	37.9	8.0	----- 29.9 -----	

* Non volatile organic

† Polyhydroxy neutral compounds

**Neutrals of high aromaticity

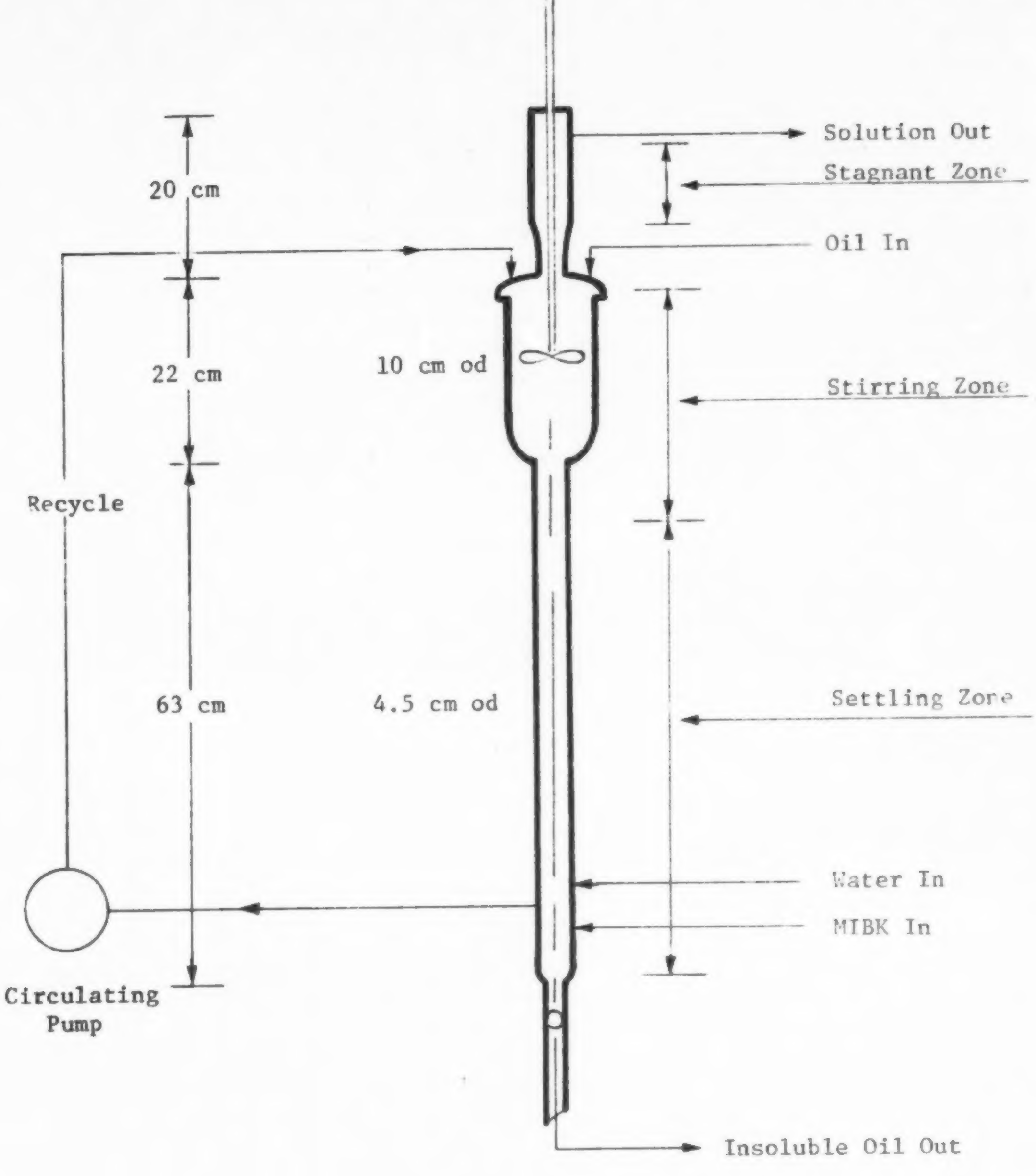
Solution Out
Stagnant Zone
20 cm
Oil In
22 cm
10 cm od
Stirring Zone
Recycle
63 cm
4.5 cm od
Settling Zone
Water In
MIBK In
Circulating Pump
Insoluble Oil Out

Figure 38. Countercurrent extractor.

the oil and solvent in the vigorously stirred zone. A recycling line was provided to withdraw a portion of the stream containing undissolved oil droplets and return it to the top of the mixing chamber. The solvent supply rate and the recycle flow rate were controlled by means of "Masterflex"* variable speed tubing pumps.

The oil sample was led through the top of the stirring chamber to a point level with the blades of a high speed propeller type stirrer. The undissolved oil droplets settled downward through the tube countercurrent to the incoming solvent stream. A portion of the rising solution phase and descending undissolved oil droplets was withdrawn through the recycle loop at a flow rate fifty times greater than the solvent intake rate and returned to the top of the stirring zone. The heavy extracted oil phase was collected and discharged at the bottom of the apparatus. The oil solution passed through a constriction at the top of the mixing chamber into the stagnant zone, and the dissolved oil stream flowed from an outlet near the top of the tube.

Process 1A. Continuous Countercurrent Water Extraction of Unstripped Oil--
The experimental procedure was as follows. The apparatus was filled with deionized water, and the stirrer and pumps were turned on. Unstripped pyrolytic oil was admitted to the apparatus. The undissolved oil was withdrawn from the bottom of the extractor and portions of the solution phase which eluted from the top of the extractor were analyzed for dissolved nonvolatile organics (NVO). The system was considered to be equilibrated when no change was observed in the NVO concentration of the successive portions of the diluted aqueous phase.

Pyrolytic oil and water were fed into the equilibrated reactor at carefully controlled rates from calibrated reservoirs. The undissolved oil phase and the diluted water solution were collected in tared receiving vessels and weighed, and the percent NVO in the oil and aqueous phases was determined. The inputs and yields from this three hour experiment are shown in TABLE 15.

The apparent loss of nonvolatile organic material was believed to be distributed between the adherent tar and the solution remaining in the extractor. The loss in water and volatile organics was attributed to evaporation and leakage.

Process 1B. Continuous Countercurrent Water Extraction of Vacuum Stripped Oil--
This experiment was conducted by the same method as Process 1A using vacuum stripped oil. The duration of the experiment was two hours and ten minutes. The inputs and yields for this experiment are summarized in TABLE 16.

---

*Cole Parmer Instrument Company, Chicago, Illinois.

TABLE 15. INPUTS AND YIELDS, PROCESS 1A

Operation	Total g	g/minute (average)
Inputs		
Oil Sample In		
Total Sample	1,998	10.8
Non Volatile Organic	1,698	9.2
Volatile Organic	140	0.8
Sample Moisture	160	0.9
Extraction Solvent In		
Water	4,120	22.3
Outputs		
Aqueous Phase	4,806	25.8
Non Volatile Organics	808	4.4
Water and Volatile Organics	3,998	44.4
Insoluble Oil Phase	1,121	6.1
Non Volatile Organics	818	4.4
Water and Volatile Organics	303	1.6
Apparent Losses		
Total	191.0	1.0
Non Volatile Organics	72.0	0.4
Water and Volatile Organics	119.0	0.6

The loss of nonvolatile organics may be attributed to trapped tars in the extractor and to dissolution in the remaining liquid phase. Evaporation is believed to be the major cause of water and volatile losses.

Process 2A. Continuous Countercurrent Three Phase Extraction of Unstripped Oil--

The apparatus was filled by pumping in approximately equal parts by volume of MIBK and water. The stirrer and recirculating pump were then turned on, and the two solvent phases were thoroughly mixed for thirty minutes. The extractor was then equilibrated by passing in constant rate streams of unstripped oil, MIBK, and water until 800 ml of oil had passed into the extractor and the NVO concentration in the effluent stream was constant. At this point the levels of oil, MIBK and water in the calibrated feed reservoirs were recorded and the effluent stream was diverted into a tared receiver. The levels of oil and solvents in the reservoirs and the weight of the receiver were recorded at approximately five minute intervals to insure constant input and output rates. At the end of 90 minutes the final oil and solvent levels and the weight of the collected effluent were

TABLE 16. INPUTS AND YIELDS, PROCESS 1B

Operation	Total g	g/minute (average)
Inputs		
Oil Sample		
Total Sample	1648	12.7
Non Volatile Organic	1621	12.5
Volatile Organic	27	0.5
Sample Moisture	0	0
Extraction Solvent In		
Water	2830	21.8
Outputs		
Aqueous Phase	3294	20.5
Non Volatile Organics	667	5.1
Water and Volatile Organics	2527	15.4
Insoluble Oil Phase	1129	8.7
Non Volatile Organics	903	6.9
Water and Volatile Organics	226	1.7
Apparent Losses		
Total		
Non Volatile Organics	57.0	0.4
Water and Non Volatile Organics	104	0.8

recorded. The effluent was a well mixed dispersion, which required overnight standing to separate into two distinct phases. No insoluble oil phase occurred. The input and yield data for this experiment are shown in TABLE 17.

Process 2B. Continuous Countercurrent Three Phase Extraction of Vacuum Stripped Oil--

This experiment was conducted with vacuum stripped oil by the same method used in Process 2A. The inputs and yields for this experiment are shown in TABLE 18.

The loss of nonvolatile organics is attributed to retention in the solution remaining in the extractor at the end of the experiment. Evaporation from the vigorously stirred system and minor leakage resulted in some loss of solvents and volatiles.

TABLE 17. INPUTS AND YIELDS, PROCESS 2A

Operation	Total g	g/minute (average)
Inputs		
Oil Sample In		
Total Sample	555	6.2
Nonvolatile Organic	472	5.2
Volatile Organic	38.9	0.4
Sample Moisture	44.1	0.5
Extraction Solvent In		
Water	780	8.7
MIBK	562	6.2
Outputs		
Aqueous Phase	1153	12.8
Nonvolatile Organics	358	4.0
Solvents and Volatile Organics	795	8.8
MIBK Phase	741	8.2
Nonvolatile Organics	114	1.3
Solvents and Volatile Organics	627	7.0
Insoluble Oil Phase	None	
Apparent Losses		
Nonvolatile Organics	0	0
Solvents and Volatile Organics	3.0	~0

Extraction of Continuous Countercurrent Aqueous Phases

The water solution from Process 1A, Process 1B, and Process 2B were exhaustively extracted with successive small portions of MIBK. The aqueous phase from Process 2A was not extracted with MIBK. The results of these extractions and the results of the subsequent analyses of the phases and fractions are summarized in TABLE 19.

The percent yields are expressed in terms of water-free oil including volatile organics. The total nonvolatile organics recovered should approach 93 percent for unstripped oil and 97 percent for vacuum stripped oil. The nonvolatile organics were approximately evenly distributed between the water phase and the insoluble oil phase in Process 1A. The solubility of the vacuum stripped oil was somewhat less than that of the unstripped oil.

In Process 2A the nonvolatile organics from the unstripped oil appeared to concentrate in the aqueous phase, and the two phases separated very slowly. These phases were stored for future applications research. In

TABLE 18. INPUTS AND YIELDS, PROCESS 2B

Operation	Total g	g/minute (average)
Inputs		
Oil Sample In		
Total Sample	1,678	13.4
Nonvolatile Organics	1,629	13.0
Volatile Organics	49	0.4
Extraction Solvents In		
Water	1,900	15.2
MIBK	1.198	9.6
Outputs		
Aqueous Phase	2,746	22.0
Nonvolatile Organics	735	5.9
Solvents and Volatile Organics	2,011	16.1
MIBK Phase	1,812	14.5
Nonvolatile Organics	798	6.4
Solvents and Volatile Organics	1,014	8.1
Insoluble Oil Phase	None	
Apparent Losses		
Nonvolatile Organics	96	0.8
Solvents and Volatile Organics	122	1.0

Process 2B , the nonvolatile organics were distributed almost equally between the aqueous and MIBK phases. Whether in water extraction (Process 1) or three phase extraction (Process 2) the presence of volatile organics enhanced the water solubility of the nonvolatile organics.

The apparent yields and distributions of phenolic compounds also were strongly dependent on the extraction method. In the water extraction experiments (Process 1) the total percent phenolic was apparently half of that detected in the three phase extraction (Process 2) products. In the three phase extraction of unstripped oil more than 80 percent of the phenolics were concentrated in the aqueous phase. With stripped oil the phenolics were distributed almost evenly between the aqueous and MIBK phases. The concentrations of polyhydroxy neutral compounds found in the water phases of Process 1A, Process 1B, and Process 2B are similar. The high apparent concentration of PNC in the Process 2 A water phase was believed to include some neutrals of high aromaticity (NHA). The solubility of NHA compounds in water was believed to be enhanced by the presence of volatile compounds from the unstripped oil. This supposition was supported by the similarity of the sums of PNC plus NHA in Process 2 A and Process 2 B. Both sums are near 56 percent.

TABLE 19. COMPOSITION OF CONTINUOUS EXTRACTION YIELDS

Process	Percent NVO*	Percent Phenolic	Percent PNC†	Percent NHA**
Process 1A (Unstripped oil)				
Aqueous Phase	44.0	9.1	26.9	8.0
Extracted Aqueous Fraction	(33.4)	(6.5)	(26.9)	(-)
MIBK Extract Fraction	(10.6)	(2.6)	(-)	(8.0)
Insoluble Oil Phase	44.5	8.4	-	36.1
Process 1B (Vacuum stripped oil)				
Aqueous Phase	40.5	6.5	28.1	5.9
Extracted Aqueous Fraction	(33.1)	(5.0)	(28.1)	(-)
MIBK Extract Fraction	(7.4)	(1.5)	-	(5.9)
Insoluble Oil Phase	54.8	7.9	-	46.9
Process 2 A (Unstripped oil)				
Aqueous Phase	70.2	31.4	38.7	-
MIBK Phase	22.3	5.9	-	16.4
Process 2 B (Vacuum stripped oil)				
Aqueous Phase	43.8	16.1	24.4	3.4
Extracted Aqueous Fraction	(35.7)	(11.4)	(24.4)	(-)
MIBK Extract Fraction	(8.1)	(4.7)	(-)	(3.4)
MIBK Phase	47.6	17.6	-	30.0

* Non volatile organics

† Polyhydroxy neutral compounds

**Neutrals of high aromaticity

Vacuum Stripping of Oil

Moisture analyses of the oil samples by azeotropic distillation with toluene indicated that about 14.7 percent of the sample was water and low boiling water soluble compounds. Gas chromatography showed 8.2 percent water and 6.5 percent volatile organics. These volatile materials could represent a possible sample cut for separate processing and could also interfere in the extraction of groups of higher molecular weight compounds in the oil. Samples of the oil were vacuum stripped in a rotary evaporator at three temperatures for varying lengths of time to determine the rate and extent of volatiles removal. Results of these experiments are shown in TABLE 20.

TABLE 20. VACUUM STRIPPING EXPERIMENTS

Temperature (°C)	Time (Hours)	P(min) Torr	Percent Volatiles Removed
23.0	40	2	13.7
23.0	60	2	13.8
53.0	0.5	24	8.2
53.0	1.0	14	11.2
53.0	4.0	2	16.4
73.0	0.4	15	9.8
73.0	0.7	2	13.8
73.0	1.0	2	15.0
73.0	2.5	2	18.7

The time required for vacuum stripping at 23°C was prohibitively long for a continuous process. Heating the oil during vacuum stripping apparently caused some chemical reactions, as the viscosity of the stripped oils increased with both increasing time and temperature.

The percent of volatiles removed in these experiments is based on the whole oil including volatiles but not water. The percent of volatiles removed was calculated from the weight of the condensate in dry ice traps between the evaporator and the vacuum pump. The thirty minute stripping operation at 53°C was chosen as the basis for a semicontinuous stripping operation to prepare oil samples for the continuous countercurrent extractions. The 8.2 percent volatiles removed included 5.1 percent water and 3.1 percent volatile organics by gas chromatography, and only minimal thickening was observed in the stripped oil.

Semicontinuous vacuum stripping experiments were carried out in Buchler Model FE-2C* continuous rotary evaporators. The unstripped oil from a calibrated reservoir was admitted to the rotating evaporator bulb immersed in a 53°C water bath and held under vacuum for 25 minutes before being aspirated to a "stripped oil" reservoir. The distilled volatiles were collected continuously in dry ice traps, and subsequently weighed and analyzed by gas chromatography. The process was repeated using 200 ml portions of unstripped oil until six liters of vacuum stripped oil had been collected. The collected volatiles totalled 8.9 percent of the dry sample weight--5.9 percent water and 3.0 percent volatile organics.

Activated Carbon Adsorption Experiments

Three experiments were run contacting water extracts of pyrolytic oil with activated carbon (Nuchar WV-G, Westvaco Carbon Co., Charleston, S.C.).

Slurry Contact with Stepwise Carbon Addition--

A 50 ml aqueous extract containing 15.9 g nonvolatile dissolved organic material was stirred vigorously and treated with successive portions of carbon until there was no further clarification of the color. After filtering and washing the carbon with water, the combined filtrate and washings were diluted with water to 100 ml. Evaporation of an aliquot portion of the residing solution indicated that 8.9 g organics remained in solution and 7.0 g had been adsorbed on the carbon.

Elution of Aqueous Extract Through Activated Carbon--

A 10 ml portion of aqueous extract containing 2.9 g dissolved organics was eluted through a 2.5 cm ID x 20 cm activated carbon column with water, 1:9 of methanol:water, 1:1 of methanol:water, methanol, and finally with carbon disulfide. The eluted fractions were collected and evaporated to dryness on a rotary vacuum evaporator. The results of this experiment are summarized in TABLE 21.

TABLE 21. ORGANICS ELUTED FROM AQUEOUS CARBON COLUMN

Fraction	Eluting Solvent	ml	Organics Eluted (g)	Total Organic Eluted (g)
D-1	Deionized Water	470	0.4405	0.4405
D-2	1:9 Methanol:Water	210	0.2892	0.7297
D-3	1:1 Methanol:Water	370	0.9968	1.7265
D-4	Methanol	650	0.5563	2.2828
D-5	Carbon Disulfide	280	0.5557*	2.8385

* Eluted as small amount of very dark methanol phase and about 265 ml of very pale carbon disulfide phase.

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*Buchler Instruments, Inc., Fort Lee, N. J.

Inspection of TABLE 21 indicates that 15 percent of the organic material eluted with water and nearly 63 percent eluted with methanol and mixtures of methanol and water. The roughly 19 percent washed from the column with carbon disulfide was concentrated in a methanol layer on top of the heavier carbon disulfide. Thus although carbon disulfide displaces the adsorbed organic material left by methanol from the activated carbon, the organic material is much more soluble in methanol than in carbon disulfide. The fractions D-1 through D-5 isolated in this experiment were analyzed by TLC, LC and IR techniques, and the results were interpreted as follows. The D-1 fraction was shown to be quite polar from the TLC and LC reversed phase column results. The IR spectra resembled the spectra of maltitol, an alcohol carbohydrate. The results of the D-2 fraction were similar to those of D-1. The data from TLC and LC with the D-3 fraction indicated the material was polar, acidic and nonaromatic. The IR spectra resembled glyoxylic acid. The TLC and LC results with D-4 indicated at least three polar components were present, and the IR spectra of one of the components resembled 3-hydroxy-4-methoxyphenylethylene glycol.

Separation of Unstripped Oil on Activated Carbon--

A 50 g sample of unstripped oil was dissolved in methanol, and a 50 ml portion of the resulting solution containing 25.1 g of nonvolatile organics was passed through a 2.5 cm ID x 50 cm carbon adsorption column, previously prepared with a methanol-carbon slurry. The eluent in 30 ml portions was returned to the top of the column until no further clarification of the solution color was observed. The column was eluted with methanol (670 ml) until the eluted liquid was nearly colorless followed by elution with 210 ml carbon disulfide. The column was eluted then by 260 ml methanol which was followed by a final elution with 100 ml of water. The results of these elutions are summarized in TABLE 22, which show that 20 percent of the organics were not eluted.

TABLE 22. ELUTION OF UNSTRIPPED OIL FROM ACTIVATED CARBON COLUMN

Elution Step	Solvent (ml)	Organic Eluted (g)	Total Organic Eluted (g)
1-Methanol	560	13.12	13.12
2-Carbon Disulfide*	210	4.99	18.11
3-Methanol	260	1.60	19.71
4-Water	100	0.40	20.11

* The eluent consisted of immiscible layers of methanol and carbon disulfide and the organic material was concentrated in immiscible methanol layer.

Slurry Contact of Aqueous Extract of Pyrolytic Oil with Activated Carbon--

A 100 ml aliquot portion of a water extract from unstripped oil containing 31.2 g dissolved nonvolatile organics was contacted with activated carbon for 3 hours. Small quantities of the liquid were removed from the mixture at intervals, filtered and evaporated at 35°C on a vacuum evaporator. These small samples indicated that the adsorption was nearly completed during the first 10 minutes. After 3 hours the carbon was filtered from the solution, washed with water, and dried. The combined filtrate and washings were evaporated to dryness in vacuo. The solutions contained 15.7 g organics (50.3 percent of the organics in the sample). The dried carbon was exhaustively extracted with N,N-dimethyl formamide (DMF), and the DMF extract contained 11.1 organics (35.6 percent of the sample). The results show that 14.1% of the organics remained on the carbon.

Acid-Base Extraction of MIBK Phase with Ether

A portion of the MIBK solution from Extraction II(4) which contained phenolics, nonvolatile hydrocarbons, and neutrals of high aromaticity was extracted with aqueous sodium hydroxide solution. The aqueous alkali extract was extracted with diethyl ether and then acidified with dilute sulfuric acid. The acidified solution was extracted with diethyl ether. The phenolics in the final diethyl ether were determined by the NAT techniques, and these results indicated that more than 90 percent of the phenolics in the original MIBK phase had been extracted.

Fractional Distillation and Analysis of Fractions

A 50 g sample of water-insoluble stripped oil, prepared by water extraction of vacuum stripped oil, was vacuum distilled at approximately 6 mm in a short path simple column apparatus. The head temperatures and yields are given in TABLE 23 below.

TABLE 23. DISTILLATION DATA FOR WATER-INSOLUBLE OIL

Fraction No.	Head Temperature (°C)	Yields (wt%)
F-1	50-100	10.5
F-2	100-110	6.3
F-3	110-120	4.6
F-4	120-175	7.9
F-5	175-193	17.3
Residue		53.4

The fractions F-1 through F-5 were examined by several analytical techniques to determine qualitatively the classes of the compounds and relative amounts. Thin layer chromatography indicated that F-1 through F-4 contained mainly two classes of compounds, phenolic aromatics and phenolic ethers. TLC indicated that F-5 contained phenolic ethers, aromatic neutrals and a trace of polyhydroxy neutral compounds. The analysis by liquid chromatography confirmed TLC findings but yielded greater resolving power among the phenolic compounds indicating F-1 and F-2 had as many as 13 compounds that were ultraviolet light absorbing. Infrared data indicate predominantly phenolics and phenolic ethers in F-1 through F-4 and aromatic neutrals mixed with phenolic ethers in F-5.

Analytical Techniques

The identification of the different classes of organic functionality has been accomplished by a variety of chemical analytical techniques. Our immediate objective in this phase has been to rapidly determine the progress of a separation process and identify the polyhydroxy compounds, dihydroxy phenolics, phenolics, phenolic ethers and neutral aromatic classes in the various phases or fractions. In most cases only a qualitative indication was needed to complete the experiment since the phenolic components were being determined by a NAT method. The fraction of neutrals of the sample was determined by difference. To determine whether the neutral fraction was primarily polyhydroxy aliphatic or aromatic or both, a TLC plate was run with carbohydrate, phenolic and phenolic ether standards. To confirm these findings an LC analysis at two wavelengths was made. An example of the results obtained from all of the techniques applied to the three different phases from a single process extraction is given in TABLE 24.

Nonaqueous Titration (NAT)--

A literature search was performed to determine suitable titration methods for total phenolic material in the presence of carboxylic acids and traces of water. Most of the conventional procedures utilized methods which allowed only anhydrous conditions for determination. Based on the literature search and experimental work, potassium hydroxide in methanol was chosen on the basis of availability, ease of preparation and stability in storage. The titration solvent chosen was dimethyl formamide because it has the required basicity and compatibility with the water, neutral compounds and phenols present in pyrolytic oils. DMF is relatively safe as compared to more volatile amines and apparently yields adequate endpoint potentiometric millivolt shifts.

Electrode systems were selected based on apparent end-point shifts in millivolts on real pyrolytic oil samples. Both a glass calomel and platinum versus platinum polarized electrode systems functioned adequately with known standards which included acetic acid, benzoic acid, phenol and guaiacol. However, the platinum polarized electrode system was the system that operated best with real pyrolytic oil samples. Standardization was accomplished with benzoic acid and guaiacol solutions, each 0.01N in DMF. The equipment used to titrate samples was a semi-automatic recording titrimeter consisting of the following components: (1) Pump - Cole Parmer Single channel, Variable speed peristaltic pump at 2.1 ml per minute; (2) Electrode - Platinum couple Fisher Scientific K-F Titrimeter electrode; (3) Polarizer - Fisher Scientific K-F Titrimeter Model 391; and (4) Recorder - Perkins Elmer Model 56.

The procedure for a determination was to standardize the semi-automatic titration equipment with 3 ml samples of standard 0.01N benzoic acid and 0.01N guaiacol solutions in DMF. Oil samples for analysis were weighed in the titrating vessel by difference. Each sample was titrated with the methanolic potassium hydroxide solution until no further endpoints were noted.

TABLE 24. ANALYTICAL RESULTS FROM BATCH EXPERIMENT PROCESS, 1A

Analytical Technique	Phases		
	Aqueous Phase extracted with MIBK	MIBK Extract of Aqueous Phase	Insoluble Oil Phase
LC	Predominately polar polyhydroxy cpds; 3 dihydroxy phenolics in moderate amts.	Predominately phenols, dihydroxy phenolics; trace of polyhydroxy cpds	Predominately aromatic neutrals; moderate amt. of phenolics and trace of polyhydroxy cpds
TLC	Main components polyhydroxy neutral cpds with 3 dihydroxy phenolics	Three phenolic cpds; only trace amts. of polyhydroxy neutrals	Strongly aromatic neutral components; moderate phenolic content; no trace of polyhydroxy cpds
NAT	6.5% phenolic 27% polyhydroxy neutrals	2.9% phenolic 6.2% neutrals	8.4% phenolic 36% neutrals
IR	Strong hydroxy functionality; strong ether functionality; weak phenolic indications	Indicated strong phenolics and ethers	Aromatic ketones; subt'd aromatics; phenolic
GC	Only small amount of sample eluted, approx. 80% of sample coked in the injector	Many phenolic and creslyic cpds	Some phenols; ether phenols
GC	Silylation of sample produced three irregular peaks of high boiling character similar to sugar cpds	-	-

In calculating the results, it was assumed that the average molecular weight of the phenolics was 125 and of the carboxylic acids, 100.

Thin Layer Chromatography--

Thin layer chromatography (TLC) offered an analytical technique which could supplement the other techniques used in this study, particularly HPLC. A separation by TLC of the general classes include the polyhydroxy carbohydrates, dihydroxy phenolics, phenolics, ether phenolics and aromatic neutrals. The TLC separations were carried out with EM Silica Gel 60F-254 plates, 20 x 20 cm, and the solvent systems and detection (visualization) reagents are given in TABLE 25.

TABLE 25. TLC SOLVENTS AND DETECTION REAGENTS

Solvent Systems

S-1*		S-2		S-3	
Ethyl acetate	65	N-butanol	40	Methanol	14
Acetonitrile	25	Acetone	50	Benzene	79
Water	10	Water	10	Water	7

Detection Reagents

D-1	D-2	D-3	D-4
Bial's Orcinol reagents used at 110°C for 5 min.	Sulfuric acid and potassium dichromate charring at 160° for 10 min.	Ultraviolet light at 254 and 365 nm	Diazotized Scarlet R Salt.

* The numbers after each solvent represents the percent by volume of each solvent in the three component system.

The general procedure for a TLC analysis was as follows. The TLC plates were normally activated for 15 min in a 110°C oven. Three microliter samples 10 mg/ml in acetonitrile were applied. Each spot was dried and the plate was developed in a presaturated tank of a chosen solvent system. After a 10 to 14 cm rise of solvent the plate was dried in a low heat oven 80°C for 10 minutes and visualized with the detection agent of choice. Inspection by U V light was usually done before any chemical reagent was applied. R_f values were calculated by conventional means using the solvent front as R_f 100 and the spotting point as R_f 0. Interpretation of the chromatograms was made using standard compounds when possible and color reactions of the various visualization reagents.

Gas Chromatography--

Gas chromatography as an analytical method was used almost exclusively in Phase III of this project to analyze the volatiles fraction, obtained from the vacuum stripping separation process. The conditions used for these analyses were:

Column 1. Pora Pak Q, 270 cm x 0.31 cm S.S.; oven, 180°C; injector, 200°C; thermal conductivity detection, 175 ma; Helium carrier at 20 ml/min
Used for the determination of water, methanol, formic acid, acetic acid, and propionic acid.

Column 2. SP-2100, 10% on HMDCS treated 100-120 mesh Supelcoport; 300 cm x 0.31 cm S.S.; FID; N_2 carrier at 20 ml/min; oven 60°C; injector 100°C;
Used for the determination of furfural.

Infrared Spectroscopy--

Infrared spectra were made of the various fractions obtained in the experiments with the continuous extraction processes. The spectra were found to contain only fragmentary information due to the multiplicity of compounds in each fraction. The overlapping of peaks precluded interpretation in only but the most general terms. Main bands of interest used in this program are given in TABLE 26.

TABLE 26. INFRARED BANDS

Micron Wavelength	Description
3.0	Broad hydrogen bonded OH function
3.8	Shoulder of carboxylic acid OH stretching
5.85 - 5.95	Carbonyl absorption
6.25 - 7.35	Carboxylate anion absorptions
10, 11, 7.1	Vinyl group absorptions
6.24, 12-14	Aromatic absorption bands

Liquid Chromatography--

Conditions used for LC analysis of fractions of the oils in this phase of the project are given in TABLE 27.

TABLE 27. LIQUID CHROMATOGRAPHY CONDITIONS

Item	Condition
Column:	Spherosol ODS C_{18} 25 cm
Solvent Gradient:	0 - 100% linear. Total time 60 min.
Solvent:	0 - 100% Acetonitrile in water
Detection:	254 nm, 190 nm
Sensitivity:	0.2 absolute
Chart speed:	8 inches per hour

SECTION 6

PILOT PLANT DESIGN

PROCESS DESCRIPTION

Pyrolysis oils contain four classes of organic compounds in addition to water which is condensed along with the organics. The classes are: phenolics, neutrals of high aromaticity (NHA), polyhydroxy aromatics, acids, and water. Separation work at the bench level led to the development of four individual processing schemes:

Process 1-A	2 Stage continuous extraction--raw oil
Process 1-B	2 Stage continuous extraction--vacuum stripped oil
Process 2-A	Continuous, simultaneous extraction--raw oil
Process 2-B	Continuous, simultaneous extraction--vacuum stripped oil

Flow sheets for the four separation process and for the combined pilot plant system are presented in Figures 39 through 43. A component-by-component description of the processes follows.

Process 1-A 2 Stage Continuous Extraction--Raw Oil

Starting at the left in Figure 39, raw pyrolytic oil, received in barrels, is pumped into the raw oil storage tank (1). In preparation for a processing run the raw oil is pumped into the raw oil feed tank (2). The raw oil feed tank is equipped with a stirrer or mixer, to provide a homogeneous feedstock. As the ambient temperature decreases the pyrolytic oil becomes more viscous. A recycle loop with a heating device is included to raise the temperature of the pyrolytic oil into the 100-130°F range, as necessary, to provide the proper flow of oil.

Raw pyrolytic oil is pumped into the extractor (3) above the mixers (near the top of the extractor). Water from the water storage tank (4) is pumped into the extractor at approximately the same height as the pyrolytic oil (and above the mixers). Two or more mixers provide violent agitation and intimate mixing of the pyrolytic oil and water. A recycle stream draws a portion of the oil-water mixture from approximately the height of the mixers and returns the mixture to the extractor near the bottom, above the level of the spent, insoluble oil. The recycle line is equipped with a heating device to raise the temperature of the mixture from ambient to about 150°F, as is necessary. Spent oil droplets descend through the extractor and accumulate in the bottom of the extractor. Excess spent, insoluble oil is pumped to the spent oil storage tank (6), while always maintaining a level of spent oil in the extractor.

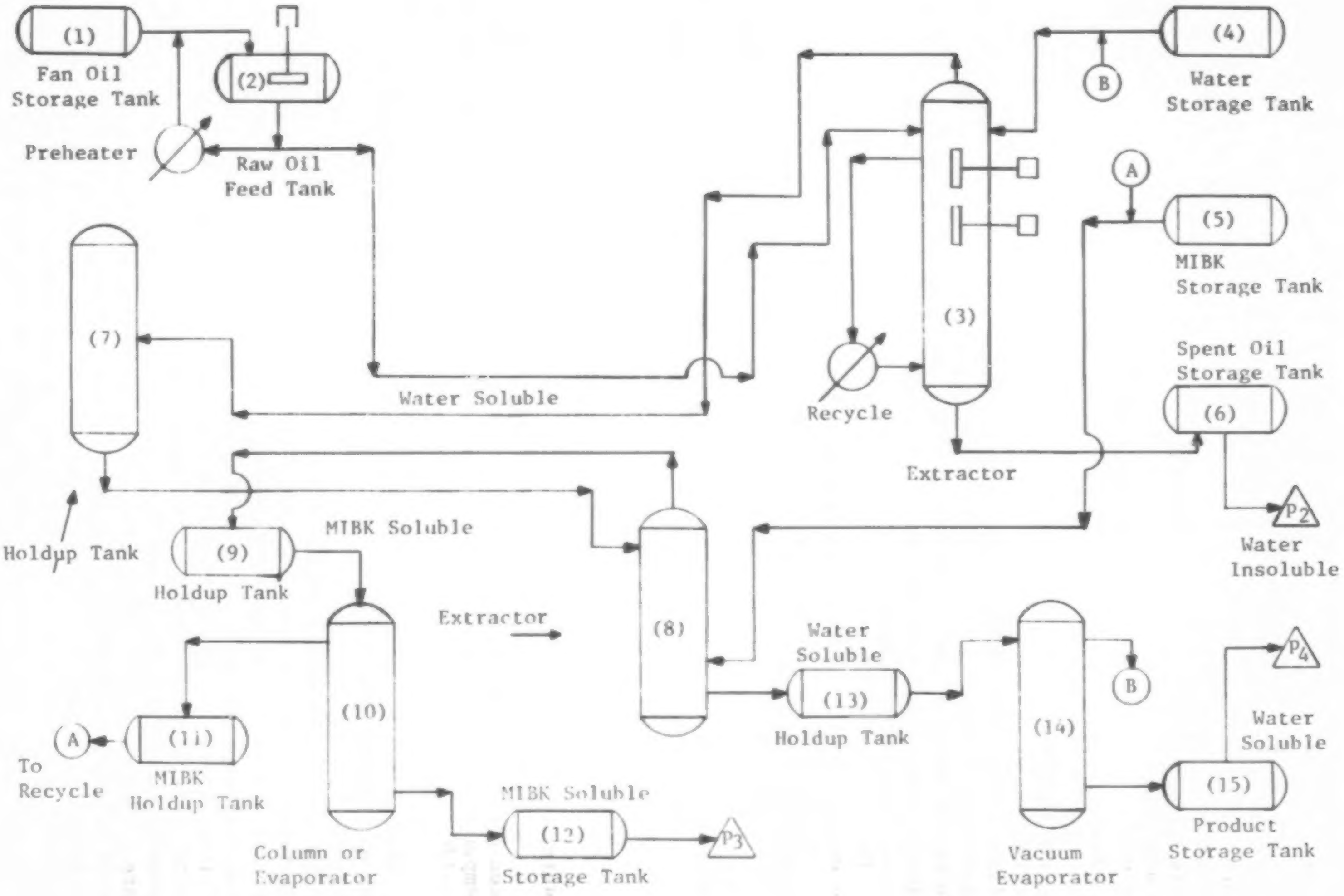
(1)
Fan Oil
Storage Tank
(2)
Preheater
Raw Oil
Feed Tank
(4)
B
Water
Storage Tank
A
(5)
MIBK
Storage Tank
(3)
Recycle
Extractor
Spent Oil
Storage Tank
(6)
P2
Water
Insoluble
(7)
Water Soluble
Holdup Tank
(9)
Holdup Tank
MIBK Soluble
Extractor
(8)
(10)
A
To
Recycle
(11)
MIBK
Holdup Tank
Column or
Evaporator
MIBK Soluble
(12)
Storage Tank
P3
Water
Soluble
(13)
Holdup Tank
(14)
B
Vacuum
Evaporator
P4
Water
Soluble
(15)
Product
Storage Tank

Figure 39. Separation process no. 1A--raw oil--2 stage extraction.

The stream of water and soluble organics exits near the top of the extractor and is pumped into a holdup tank (7). The material in the holdup tank is pumped into the 2nd stage extractor (8) at a level above the mixers. Methyl isobutyl ketone (MIBK) is pumped into the extractor from the MIBK storage tank (5), at approximately the same level as the water soluble organic inlet stream. Two or more mixers or stirrers provide violent agitation and intimate mixing of the water soluble organics and the MIBK. A recycle stream draws a portion of the water soluble organic--solvent mixture from the level of the mixers and returns the mixture to the extractor near the bottom. A phase separation occurs in the extractor, with the heavier aqueous solution settling to the bottom of the extractor, and the lighter organic solution moving toward the top of the extractor. The aqueous solution is removed from the extractor near the bottom and is pumped into the water soluble holdup tank (13), and then into the vacuum evaporator (14) where the water soluble organics are separated from the water. The water is vaporized and returned to the water storage tank (4). The organics are pumped into the water soluble organics--product storage tank (15).

The organic phase from the second stage extractor exits near the top of the extractor and is pumped into the MIBK soluble holdup tank (9). The organic phase is then fed into an evaporator (or column) (10) where the MIBK is vaporized and collected in the MIBK-holdup tank (11). The recovered MIBK is then returned to the MIBK storage tank (5). The MIBK soluble organics are concentrated in the evaporator and pumped to the MIBK soluble organics--product storage tank (12).

Process 1-B 2 Stage Continuous Extractor--Vacuum Stripped Oil

Starting at the left in Figure 40, raw pyrolytic oil, received in barrels, is pumped into the raw oil storage tank (1). In preparation for a processing run the raw oil is pumped into the raw oil feed tank (2). The raw oil feed tank is equipped with a stirrer or mixer, to provide a homogeneous feed stock. A recycle loop with a heating device is included to raise the temperature of the pyrolytic oil into the 100-130°F range, as necessary, to provide the proper flow of oil.

The raw pyrolytic oil is pumped into a vacuum evaporator (or vacuum stripping column) (3), to remove the volatiles. The volatiles are components that are vaporized at atmospheric pressure at 100°F (212°F). They consist of water (60-70%), acetic acid ($\approx$ 20%) and small amounts of other low boiling organic compounds. The volatiles are condensed and pumped to the volatiles storage tank (4). The vacuum stripped oil is pumped from the stripper to the 1st stage extractor (5), and enters the extractor above the mixers (near the top of the extractor). Water from the water storage tank (6) is pumped into the extractor at approximately the same height as the vacuum stripped oil (and above the mixers). Two or more mixers provide violent agitation and intimate mixing of the vacuum stripped oil and water. A recycle stream draws a portion of the oil-water mixture from approximately the height of the mixers and returns the mixture to the extractor near the bottom, above the level of the spent insoluble oil. The recycle line is equipped with a heating device to raise the temperature of the mixture from ambient to about 150°F,

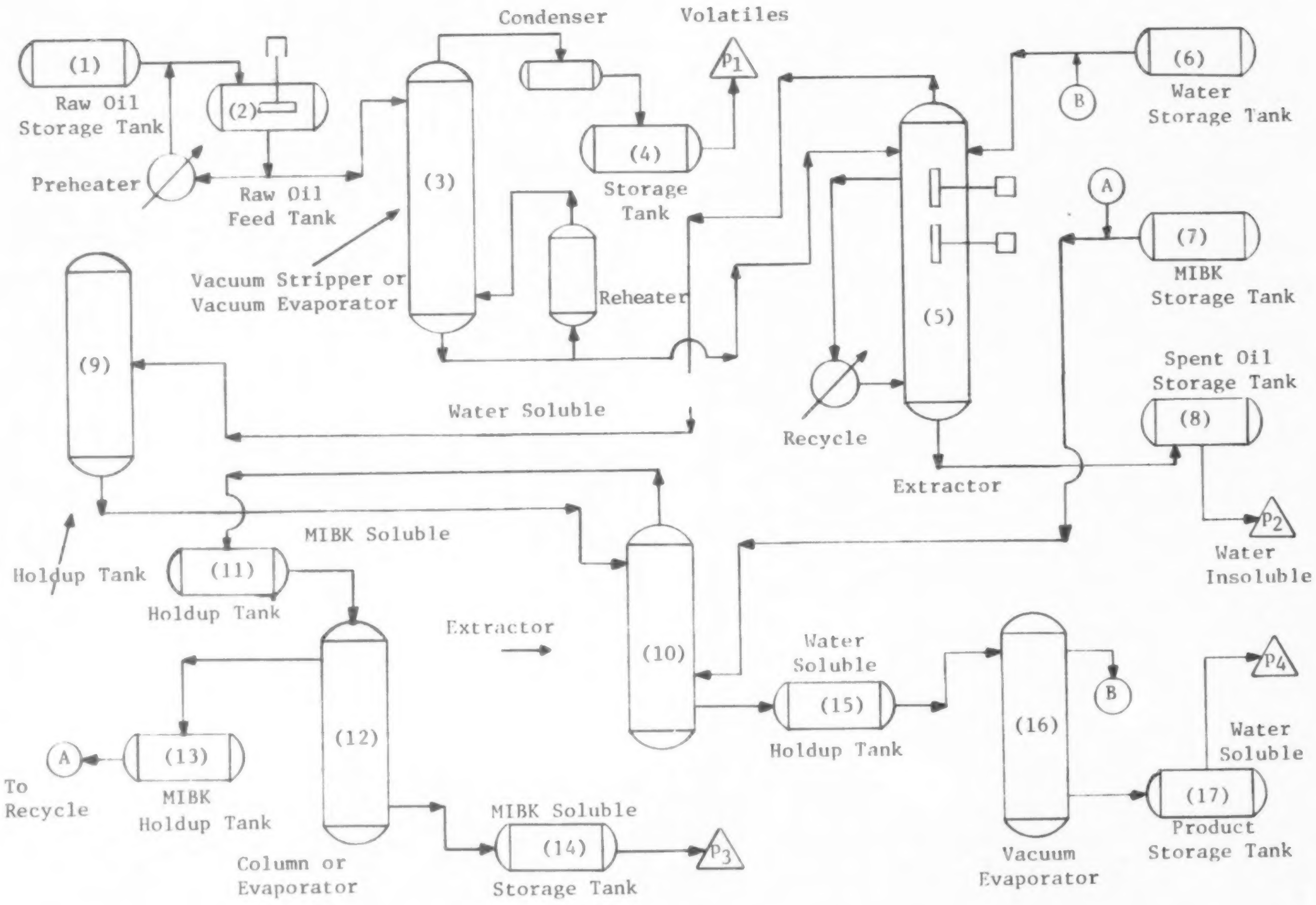
(1)
Raw Oil
Storage Tank
(2)
Preheater
Raw Oil
Feed Tank
Condenser
Volatiles
P_1
(3)
(4)
Storage
Tank
Vacuum Stripper or
Vacuum Evaporator
Reheater
(6)
Water
Storage Tank
B
(5)
A
(7)
MIBK
Storage Tank
(9)
Water Soluble
Recycle
Spent Oil
Storage Tank
(8)
Extractor
P_2
Water
Insoluble
Holdup Tank
(11)
MIBK Soluble
Holdup Tank
Extractor
(10)
Water
Soluble
(15)
Holdup Tank
(16)
B
P_4
Water
Soluble
(12)
A
To
Recycle
(13)
MIBK
Holdup Tank
Column or
Evaporator
MIBK Soluble
(14)
Storage Tank
P_3
Vacuum
Evaporator
(17)
Product
Storage Tank

Figure 40. Separation process 1B--vacuum stripped--2 stage extraction.

as is necessary. Spent oil droplets descend through the extractor and accumulate in the bottom of the extractor. Excess, spent insoluble oil is pumped to the spent oil storage tank (8), while always maintaining a level of spent oil in the extractor.

The stream of water and soluble organics exits near the top of the extractor and is pumped into a holdup tank (9). The material in the holdup tank is pumped into the 2nd stage extractor (10) at a level above the mixers. Methyl isobutyl ketone (MIBK) is pumped into the extractor from the MIBK storage tank (7), at approximately the same level as the water soluble organic inlet stream. Two or more mixers or stirrers provide violent agitation and intimate mixing of the water soluble organics and the MIBK. A recycle stream draws a portion of the water soluble organic--solvent mixture from the level of the mixers and returns the mixture to the extractor near the bottom. A phase separation occurs in the extractor, with the heavier aqueous solution settling to the bottom of the extractor, and the lighter organic solution moving toward the top of the extractor. The aqueous solution is removed from the extractor near the bottom and is pumped into the water soluble holdup tank (15), and then into the vacuum evaporator (16) where the water soluble organics are separated from the water. The water is vaporized and returned to the water storage tank (6). The organics are pumped into the water soluble organics--product storage tank (17).

The organic phase from the second stage extractor exits near the top of the extractor and is pumped into the MIBK soluble-holdup tank (11). The organic phase is then fed into an evaporator (or column) (12) where the MIBK is vaporized and then collected in the MIBK-Holdup tank (13). The recovered MIBK is then returned to the MIBK storage tank (7). The MIBK soluble organics are concentrated in the evaporator and pumped to the MIBK soluble organics--product storage tank (14).

Process 2-A Continuous, Simultaneous Extraction--Raw Oil

Starting at the left in Figure 41, raw pyrolytic oil, received in barrels, is pumped into the raw oil storage tank (1). In preparation for a processing run the raw oil is pumped into the raw oil feed tank (2). The raw oil feed tank is equipped with a stirrer or mixer, to provide a homogeneous feedstock. As the ambient temperature decreases the pyrolytic oil becomes more viscous. A recycle loop with a heating device is included to raise the temperature of the pyrolytic oil into the 100-130°F range, as necessary, to provide the proper flow of oil.

Raw pyrolytic oil is pumped into the extractor (3) above the mixers (near the top of the extractor). Water from the water storage tank (4) is pumped into the extractor at approximately the same height as the pyrolytic oil (and above the mixers). MIBK is pumped into the extractor from the MIBK storage tank (5) at a level below the mixers. Two or more mixers provide violent agitation and intimate mixing of the pyrolytic oil, water, and MIBK. A recycle stream draws a portion of the oil-water-MIBK mixture from approximately the height of the mixers and returns the mixture to the extractor near the bottom. The recycle line is equipped with a heating device to raise the temperature of the mixture from ambient to about 150°F, as is necessary.

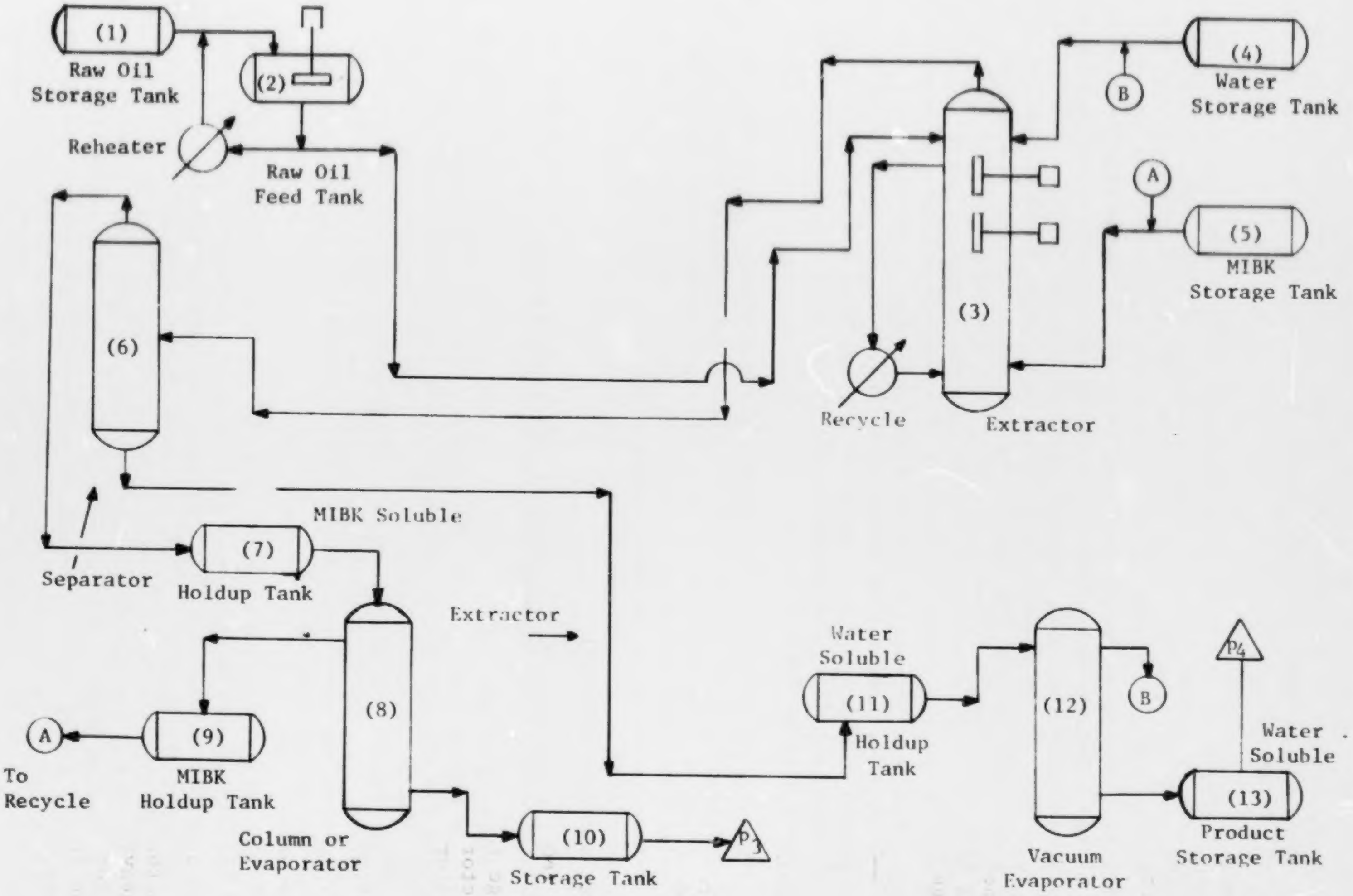
(1)
Raw Oil
Storage Tank
(2)
Reheater
Raw Oil
Feed Tank
(4)
Water
Storage Tank
B
A
(5)
MIBK
Storage Tank
(3)
Recycle
Extractor
(6)
MIBK Soluble
Separator
(7)
Holdup Tank
Extractor
(8)
Column or
Evaporator
A
To
Recycle
(9)
MIBK
Holdup Tank
(10)
Storage Tank
P_3
Water
Soluble
(11)
Holdup
Tank
(12)
Vacuum
Evaporator
B
P_4
Water
Soluble
(13)
Product
Storage Tank

Figure 41. Separation process 2A--raw oil--simultaneous extraction.

The oil-water-MIBK mixture exits near the top of the extractor and is pumped into a separator (6). A phase separation occurs, with the heavier aqueous solution settling to the bottom, and the lighter organic solution moving toward the top of the separator. The aqueous solution is pumped from the separator to the water soluble holdup tank (11), and then into the vacuum evaporator (12) where the water soluble organics are separated from the water. The water is vaporized and returned to the water storage tank (4). The organics are pumped into the water soluble organics--product storage tank (13).

The organic phase from the separator exits from the top of the separator and is pumped into the MIBK soluble-holdup tank (7). The organic phase is then fed into an evaporator (or column) (8) where the MIBK is vaporized and collected in the MIBK holdup tank (9). The recovered MIBK is then returned to the MIBK storage tank (5). The MIBK soluble organics are concentrated in the evaporator and pumped to the MIBK soluble organics--product storage tank (10).

Process 2-B Continuous, Simultaneous Extraction--Vacuum Stripped Oil

Starting at the left in Figure 42, raw pyrolytic oil, received in barrels, is pumped into the raw oil storage tank (1). In preparation for a processing run the raw oil is pumped into the raw oil feed tank (2). The raw oil feed tank is equipped with a stirrer or mixer, to provide a homogeneous feedstock. A recycle loop with a heating device is included to raise the temperature of the pyrolytic oil into the 100-130°F range, as necessary, to provide the proper flow of oil.

The raw pyrolytic oil is pumped into a vacuum evaporator (or vacuum stripping column) (3), to remove the volatiles. The volatiles are components that are vaporized at atmospheric pressure at 100°F (212°F). They consist of water (60-70%), acetic acid (≈20%) and small amounts of other low boiling organic compounds. The volatiles are condensed and pumped to the volatiles storage tank (4). The vacuum stripped oil is pumped from the stripper to the extractor (5), above the mixers (near the top of the extractor). Water from the water storage tank (6) is pumped into the extractor at approximately the same height as the vacuum stripped oil (and above the mixers). MIBK is pumped into the extractor from the MIBK storage tank (7) at a level below the mixers. Two or more mixers provide violent agitation and intimate mixing of the vacuum stripped oil, water and MIBK. A recycle stream draws a portion of the oil-water-MIBK from approximately the height of the mixers and returns the mixture to the extractor near the bottom. The recycle line is equipped with a heating device to raise the temperature of the mixture from ambient to about 150°F, as is necessary.

The vacuum stripped oil-water-MIBK mixture exits near the top of the extractor and is pumped into a separator (8). A phase separation occurs, with the heavier aqueous solution settling to the bottom, and the lighter organic solution moving toward the top of the separator. The aqueous solution is pumped from the separator to the water soluble holdup tank (13), and then into the vacuum evaporator (14) where the water soluble organics are separated from the water. The water is vaporized and returned to the water storage tank (6).

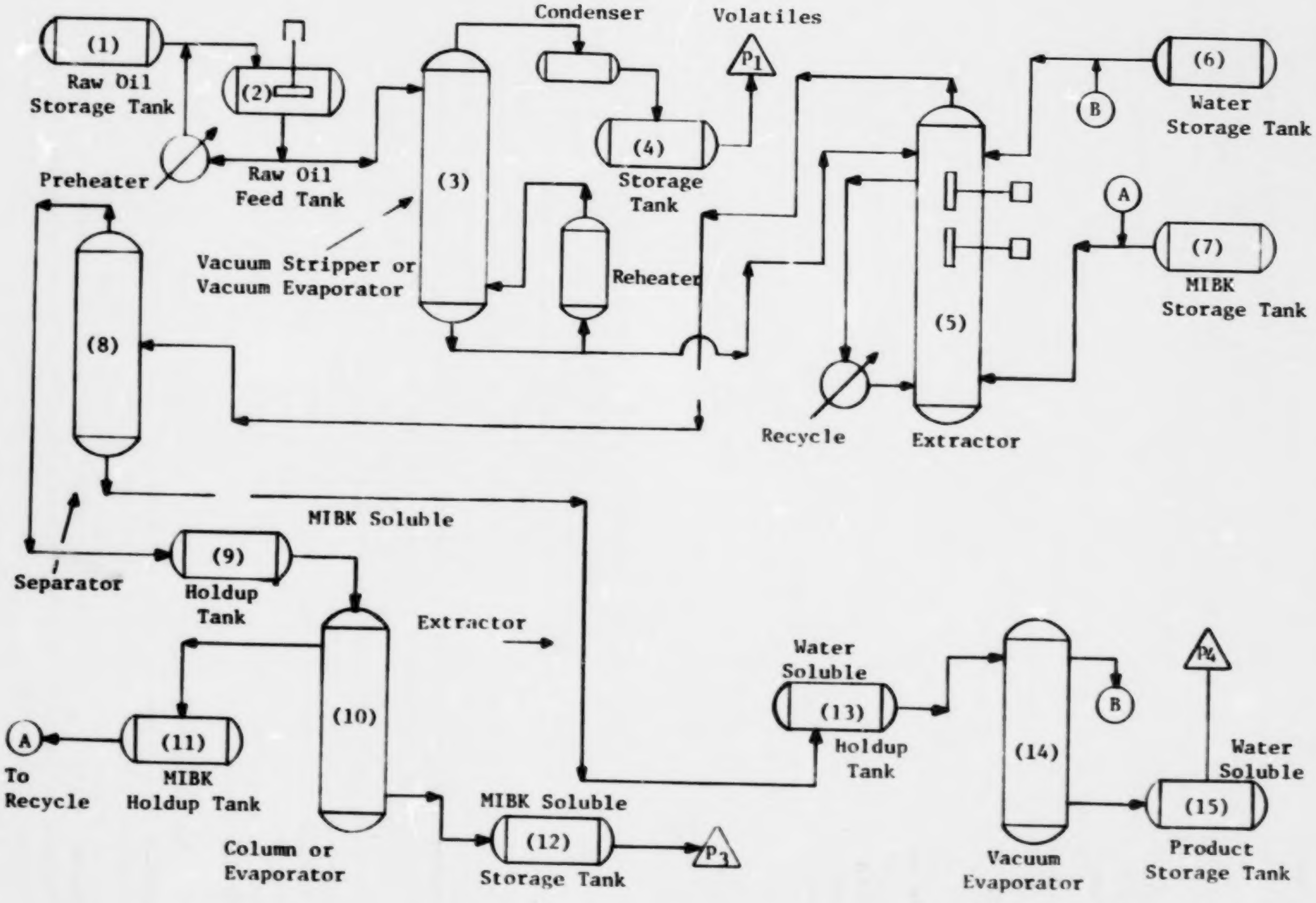
(1)
Raw Oil
Storage Tank
(2)
Raw Oil
Feed Tank
Preheater
Condenser
Volatiles
P_1
(3)
Vacuum Stripper or
Vacuum Evaporator
(4)
Storage
Tank
Reheater
(5)
Extractor
Recycle
(6)
Water
Storage Tank
B
A
(7)
MIBK
Storage Tank
(8)
Separator
MIBK Soluble
(9)
Holdup
Tank
Extractor
(10)
Column or
Evaporator
(11)
MIBK
Holdup Tank
A
To
Recycle
MIBK Soluble
(12)
Storage Tank
P_3
Water
Soluble
(13)
Holdup
Tank
(14)
Vacuum
Evaporator
B
P_4
Water
Soluble
(15)
Product
Storage Tank

Figure 42. Separation process 2B--vacuum stripped--simultaneous extraction.

The organics are pumped into the water soluble organics - product storage tank (15).

The organic phase from the separator exits from the top of the separator and is pumped into the MIBK soluble-holdup tank (9). The organic phase is then fed into an evaporator (or column) (10), where the MIBK is vaporized and collected in the MIBK holdup tank (11). The recovered MIBK is then returned to the MIBK storage tank (7). The MIBK soluble organics are concentrated in the evaporator and pumped to the MIBK soluble organics-product storage tank (12).

DESIGN OF THE PILOT PLANT

The pilot plant processing scheme, in each of the four cases is based on the results of the batch and continuous extraction data produced during the laboratory experiments. Pilot equipment must be large enough to provide the data necessary to accurately scale up to design a commercial pyrolytic oil processing plant. But a major constraint on the size of the pilot plant is the availability of the pyrolytic oil. The basis for the sizing of the pilot plant is given below. (See Appendices A and B for calculations.)

Size of Pilot Plant

The proportions of the input and output streams for the four cases of the pilot plane design are determined by the rate data provided by the lab scale continuous extraction data. To arrive at a flowrate for pilot plant use, the actual residence time for each extraction method is inspected. TABLE 28 shows the input rates in grams per minute and ml per minute for each component, the total volume flowrate in ml per minute, the extractor volume in ml , and the residence time in minutes.

TABLE 28 . INPUT RATES TO EXTRACTOR

	Input Rate grams/min			Input Rate ml/min			Total Input Rate	Extractor Volume	Residence Time
Process	Oil	Water	MIBK	Oil	Water	MIBK	ml/min	ml	Min.
1-A	10.60	22.34	--	8.72	22.34	--	31.06	1950	62.77
1-B	13.10	23.30	--	10.58	23.30	--	33.88	1950	57.56
2-A	6.19	9.39	6.18	5.02	9.39	7.72	22.13	1950	88.13
2-B	13.28	15.54	9.75	10.73	15.54	12.17	38.44	1950	50.73

Choosing a minimum residence time of 65 minutes, TABLE 29 shows the required extractor volume for various oil input rates and total input rates.

TABLE 29. REQUIRED EXTRACTOR VOLUME

Input Rate GPM	Total Input Rate GPM	Extractor Volume Gal.	Minimum Oil Input Rate Gal.
3	9	588	195
4	12	780	260
5	15	975	325
6	18	1170	390

As calculated from TABLE 29 the oil input rate (in ml per minute) is approximately 1/3 of the total input rate (ml per min). The oil input rate for the pilot plant design was selected to be 4 GPM.

COST SUMMARY

The costs for the major equipment necessary to conduct tests using any of the 4 processing schemes is shown in TABLE 30. The total installed equipment cost is $365,900. The pilot plant equipment cost including instrumentation and controls, electrical, and piping is $508,000. (See Appendix B).

TABLE 30. PILOT PLANT - COST SUMMARY

Raw Oil Storage Tank	(1)	$9,382
Raw Oil Feed Tank	(2)	9,382
Vacuum Evaporator (Stripper)	(3)	39,090
Extractor (1st Stage)	(4)	48,790
Separator (or Holdup Tank	(5)	23,454
Extractor (2nd Stage)	(6)	48,790
MIBK Soluble - Holdup Tank	(7)	9,382
Evaporator	(8)	46,908
MIBK Holdup Tank	(9)	3,440
MIBK Soluble - Product Storage Tank	(10)	4,691
Water Soluble - Holdup Tank	(11)	9,382
Vacuum Evaporator	(12)	87,561
Water Soluble - Product Storage Tank	(13)	7,193
MIBK Storage Tank	(14)	3,440
Volatiles - Product Storage Tank	(15)	4,691
Spent Oil - Product Storage Tank	(16)	4,691
Water Storage Tank	(17)	5,629
Total Installed Equipment Cost		365,900
Instrumentation and Controls (9.35% of installed equipment cost)		34,200
Piping - (22.3% of installed equipment cost)		81,600
Electrical - (7.2% of installed equipment cost)		26,300
Total Pilot Plant Equipment Cost		$508,000

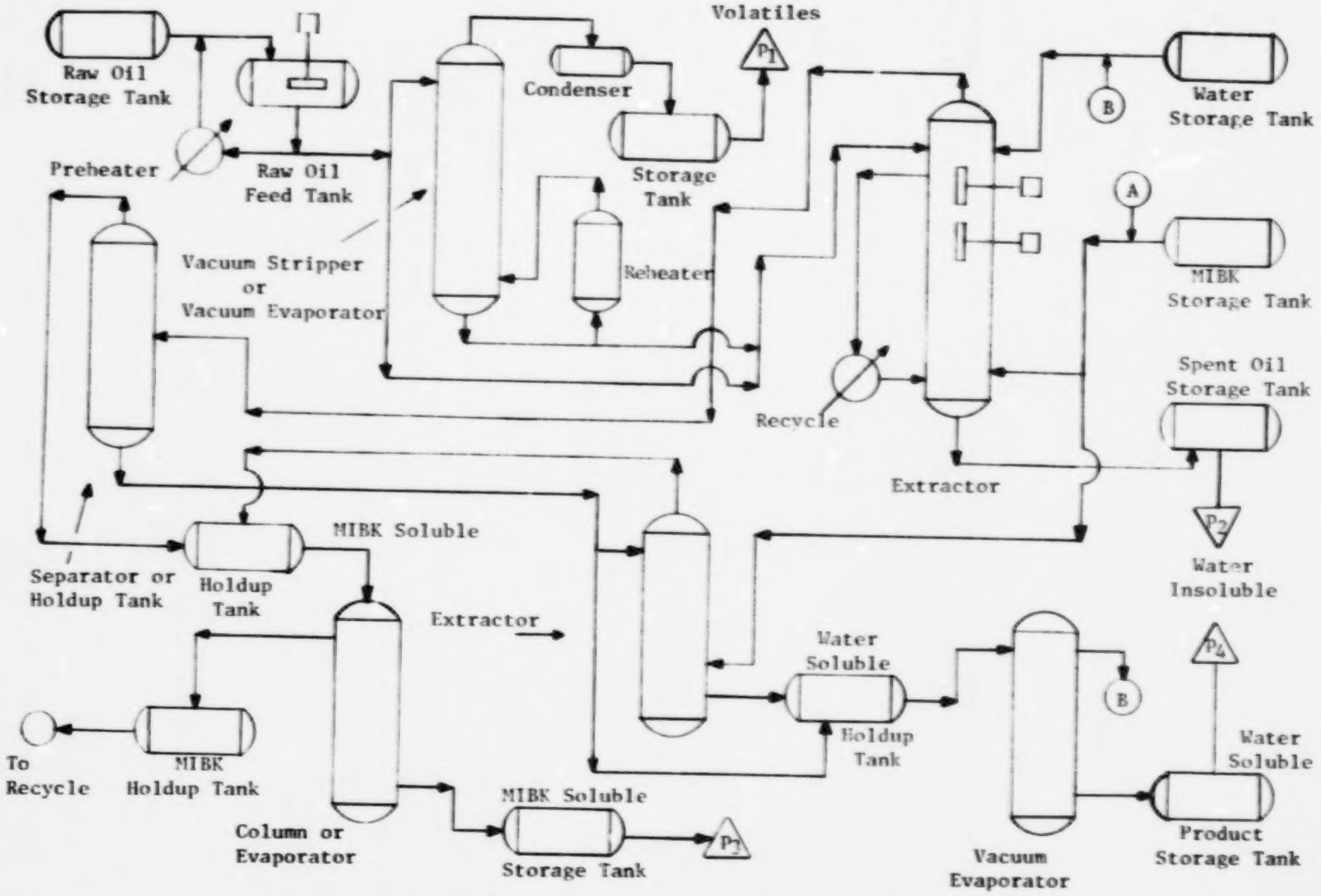
Raw Oil Storage Tank
Preheater
Raw Oil Feed Tank
Vacuum Stripper or Vacuum Evaporator
Condenser
Storage Tank
Volatiles
P1
Reheater
Recycle
Extractor
Water Storage Tank
B
A
MIBK Storage Tank
Spent Oil Storage Tank
P2
Water Insoluble
Separator or Holdup Tank
Holdup Tank
MIBK Soluble
Extractor
Water Soluble
Holdup Tank
B
P4
Water Soluble
To Recycle
MIBK Holdup Tank
Column or Evaporator
MIBK Soluble Storage Tank
P3
Vacuum Evaporator
Product Storage Tank

Figure 43. Pyrolysis oil pilot plant schematic--continuous process.

SECTION 7

DESIGN AND ECONOMICS OF COMMERCIAL SIZE PLANT

PROCESS DESCRIPTION

The four processing schemes examined at the pilot plant scale are further investigated at the size of a commercial facility. A component by component description of the four processes is given in Section 6. Flow sheets for the four separation processes are shown in Figures 39 through 42. At this preliminary stage of the process design, the commercial size plant and the pilot plant differ only in the size of the major process equipment. The process descriptions remain the same.

DESIGN BASIS

The full scale, commercial pyrolytic oil processing plant is based on the availability of pyrolytic oil. The oil will be provided by one or more wood pyrolysis plants. It is possible that future pyrolytic oil processing plants will use oil produced from sources other than wood - other agricultural or cellulosic materials, or municipal refuse - but for the purposes of this design only wood pyrolysis will be considered.

Georgia Tech has had considerable experience with the Georgia Tech - Tech-Air Corporation pyrolysis system, which produces char and pyrolytic oil by the pyrolysis of wood. Although other processes are available to produce pyrolytic oil, no other process has performed reliably on a continuous basis over an extended period of time. The Tech-Air Corporation has operated a pyrolysis plant, using the Georgia Tech - Tech-Air process over a period of several years in South Georgia. That plant had a nominal processing rate of 1-1/2 to 2 tons per hour of dried wood material. In addition the Stanford Research Institute (SRI) stated that the Georgia Tech - Tech-Air technology was the closest to commercialization of all the processes investigated [24]. Therefore, the Georgia Tech Pyrolysis Process [6] will be used as a basis for the supply of pyrolytic oil.

Preliminary design calculations have been made to scale the Georgia Tech pyrolysis process up to anywhere from 3.5 tons per hour to several hundred tons per hour, based on a dried wood feed material. SRI uses a plant size of 1,000 ton per day, dry wood feed rate, or approximately 42 tons per hour. The SRI study used four 10 ton per hour (dry feed rate) pyrolyzers operating in parallel.

Since the size of the largest operating pyrolysis plant to date is only 1-1/2 to 2 tons of dried feed per hour, it is not likely that the next generation of pyrolyzers will be scaled up to 10 tons per hour. An intermediate size in the range of 3.5 to 7 tons per hour will probably be built and tested for a period of time. It is estimated that the data currently available will permit the construction of a nominal 5 ton per hour pyrolyzer with limited risk regarding performance. It has been projected that 5 ton per hour pyrolyzer is large enough to adequately provide a return on the capital investment, while minimizing the unknowns associated with scale up.

Therefore it is projected that five 5 ton per hour (dry feed rate) pyrolysis plants will provide oil to the pyrolytic oil processing plant. The pyrolysis plants are estimated to operate with an 18% oil yield based on the dry feed rate to the pyrolyzers, with an operating year of 345 days. Thus the oil processing plant must be located in proximity to 25 tons per hour of pyrolysis processing capacity. This requirement is conservative when compared to the SRI scenario of individual pyrolysis plants of 42 tons per hour. Based on the conditions above, one 5 ton per hour pyrolysis plant will produce 14,904,000 pounds of oil per operating year or 1,419,400 gallons per year. The combined output of the 5 pyrolysis plants is 74,520,000 pounds per year or 7,097,000 gallons per year.

ECONOMICS AND FEASIBILITY

The economic feasibility of each process discussed in Section 6 has been considered for a commercial size plant. This analysis included total capital investment with equipment costs, manufacturing and product costs, depreciation and estimated income.

Itemized equipment costs and equipment sizing calculations are included in Appendix C. Each of the processes (1A, 1B, 2A, 2B) were treated as a separate case. Cost summaries for the major equipment for each of the processes are given in Appendix C and in TABLES 31-34. The total installed equipment costs for each of the processes are: 1A, $1,127,000; 1B, $1,172,000; 2A, $1,025,000; and 2B, $1,036,000. The equipment costs are included in the direct costs of the total capital investment.

The total capital investment, which included direct and indirect costs and working capital, were calculated for each process and are summarized on pages 93-96. The manufacturing and total product costs which include raw materials, labor, utilities, maintenance, operating supplies, laboratory costs and direct production costs are summarized on pages 97-100. Depreciation is discussed on pages 101-102.

In order to arrive at estimated current selling prices for potential chemical fractions from pyrolytic oil, prices for similar organic substances were selected and used from the Chemical Marketing Reporter of December, 1979. Income was calculated for a minimum, average and maximum selling price, and these results are summarized on pages 102-107. The rate of return analysis is presented on pages 107-116.

TABLE 31. PROCESS 1A - 2 STAGE CONTINUOUS EXTRACTION - RAW OIL - INSTALLED EQUIPMENT COST SUMMARY

Raw Oil Storage Tank	(1)	$187,600
Raw Oil Feed Tank	(2)	9,400
Extractor - 1st Stage	(3)	91,500
Water Storage Tank	(4)	31,300
MIBK Storage Tank	(5)	8,100
Spent Oil Storage Tank	(6)	136,100
Holdup Tank	(7)	39,100
Extractor - 2nd Stage	(8)	99,100
MIBK Soluble - Holdup Tank	(9)	31,300
Evaporator	(10)	71,300
MIBK Holdup Tank	(11)	31,300
MIBK Soluble - Product Storage Tank	(12)	50,000
Water Soluble - Holdup Tank	(13)	41,900
Vacuum Evaporator	(14)	187,600
Water Soluble - Product Storage Tank	(15)	111,000
Total Installed Equipment Cost		$1,126,600

TABLE 32. PROCESS 1B - 2 STAGE CONTINUOUS EXTRACTION - VACUUM STRIPPED OIL-INSTALLED EQUIPMENT COST SUMMARY

Raw Oil Storage Tank	(1)	$187,600
Raw Oil Feed Tank	(2)	9,400
Vacuum Evaporator - Raw Oil	(3)	78,200
Volatiles Storage Tank	(4)	73,500
Extractor - 1st Stage	(5)	77,800
Water Storage Tank	(6)	46,900
MIBK Storage Tank	(7)	7,500
Spent Oil Storage Tank	(8)	139,500
Holdup Tank	(9)	36,000
Extractor - 2nd Stage	(10)	80,800
MIBK Soluble - Holdup Tank	(11)	29,100
Evaporator	(12)	51,600
MIBK Holdup Tank	(13)	28,100
MIBK Soluble - Product Storage Tank	(14)	39,100
Water Soluble - Holdup Tank	(15)	36,900
Vacuum Evaporator	(16)	150,100
Water Soluble - Product Storage Tank	(17)	100,000
Total Installed Equipment Cost		$1,172,100

TABLE 33. PROCESS 2A - CONTINUOUS, SIMULTANEOUS EXTRACTION - RAW OIL - INSTALLED EQUIPMENT COST SUMMARY

Raw Oil Storage Tank	(1)	$187,600
Raw Oil Feed Tank	(2)	9,400
Extractor	(3)	120,400
Water Storage Tank	(4)	46,900
MIBK Storage Tank	(5)	8,100
Separator	(6)	55,400
MIBK Soluble - Holdup Tank	(7)	36,600
Evaporator	(8)	100,100
MIBK Holdup Tank	(9)	31,300
MIBK Soluble - Product Storage Tank	(10)	79,400
Water Soluble - Holdup Tank	(11)	40,700
Vacuum Evaporator	(12)	156,400
Water Soluble - Product Storage Tank	(13)	153,200
Total Installed Equipment Cost		$1,025,500

TABLE 34. PROCESS 2B - CONTINUOUS, SIMULTANEOUS EXTRACTION - VACUUM STRIPPED OIL - INSTALLED EQUIPMENT COST SUMMARY

Raw Oil Storage Tank	(1)	$187,600
Raw Oil Feed Tank	(2)	9,400
Vacuum Evaporator	(3)	78,200
Volatiles Storage Tank	(4)	73,500
Extractor	(5)	83,900
Water Storage Tank	(6)	37,500
MIBK Storage Tank	(7)	6,900
Separator	(8)	41,900
MIBK Soluble - Holdup Tank	(9)	28,100
Evaporator	(10)	65,700
MIBK Holdup Tank	(11)	23,400
MIBK Soluble - Product Storage Tank	(12)	111,000
Water Soluble - HOldup Tank	(13)	36,000
Vacuum Evaporator	(14)	134,500
Water Soluble - Product Storage Tank	(15)	118,800
Total Installed Equipment Cost		$1,036,400

Total Capital Investment

Direct Costs--Process 1-A 2 Stage Continuous Extraction--Raw Oil

Purchased Equipment--Installed (End '79)	$1,126,600
Instrumentation and Controls--Installed - 9.35% of Installed Equipment Costs	105,300
Piping--Installed - 22.3% of Installed Equipment Costs	251,200
Electrical--Installed - 7.2% of Installed Equipment Costs	81,100
Buildings--Including Services - 20.8% of Installed Equipment Costs	234,300
Yard Improvements - 7.2% of Installed Equipment Costs	81,100
Service Facilities--Installed - 39.6% of Installed Equipment Costs	446,100
Total Direct Plant Cost	$2,325,700

Indirect Costs--

Engineering and Supervision - 25.2% of Installed Equipment Costs	$ 283,900
Construction Expense - 20.9% of Installed Equipment Costs	235,500
Total Direct and Indirect Costs	$2,845,100
Contractor's Fee - 5% of Direct and Indirect Costs	142,300
Contingency - 10% of Direct and Indirect Costs	284,500
Fixed Capital Investment	3,271,900
Working Capital - 10% of Total Capital Investment	363,500
Total Capital Investment	$3,635,400

Direct Costs--Process 1B--2 Stage Continuous Extraction--Vacuum Stripped Oil

Purchased Equipment--Installed (End '79)	$1,172,100
Instrumentation and Controls--Installed - 9.35% of Installed Equipment Costs	109,600
Piping--Installed - 22.3% of Installed Equipment Costs	261,400
Electrical--Installed - 7.2% of Installed Equipment Costs	84,400
Buildings--Including Services - 20.8% of Installed Equipment Costs	243,800
Yard Improvements - 7.2% of Installed Equipment Costs	84,400
Service Facilities--Installed - 39.6% of Installed Equipment Costs	464,100
Total Direct Plant Cost--	2,419,800
Indirect Costs--	
Engineering and Supervision - 25.2% of Installed Equipment Costs	295,400
Construction Expense - 20.9% of Installed Equipment Costs	244,900
Total Direct and Indirect Costs	2,960,100
Contractor's Fee - 5% of Direct and Indirect Costs	148,000
Contingency - 10% of Direct and Indirect Costs	296,000
Fixed Capital Investment	3,404,100
Working Capital - 10% of Total Capital Investment	378,200
Total Capital Investment	$3,782,300

Direct Costs--Process 2A--Continuous, Simultaneous Extraction--Raw Oil	
Purchased Equipment--Installed (End '79)	$1,025,500
Instrumentation and Controls--Installed - 9.35% of Installed Equipment Costs	95,900
Piping--Installed - 22.3% of Installed Equipment Costs	228,700
Electrical--Installed - 7.2% of Installed Equipment Costs	73,800
Buildings--Including Services - 20.8% of Installed Equipment Costs	213,300
Yard Improvements - 7.2% of Installed Equipment Costs	73,800
Services Facilities--Installed - 39.6% of Installed Equipment Costs	406,100
Total Direct Plant Cost--	$2,117,100
Indirect Costs	
Engineering and Supervision - 25.2% of Installed Equipment Costs	258,400
Construction Expense - 20.9% of Installed Equipment Costs	214,300
Total Direct and Indirect Costs	2,589,800
Contractor's Fee - 5% of Direct and Indirect Costs	129,500
Contingency - 10% of Direct and Indirect Costs	259,000
Fixed Capital Investment	2,978,300
Working Capital - 10% of Total Capital Incestment	330,900
Total Capital Investment	$3,309,200

Direct Costs--Process 2B--Continuous, Simultaneous Extraction--Vacuum Stripped Oil

Purchased Equipment--Installed (End '79)	$1,036,400
Instrumentation and Controls--Installed - 9.35% of Installed Equipment Costs	96,900
Piping--Installed - 22.3% of Installed Equipment Costs	231,100
Electrical--Installed - 7.2% of Installed Equipment Costs	74,600
Buildings--Including Services - 20.8% of Installed Equipment Costs	215,600
Yard Improvements - 7.2% of Installed Equipment Costs	74,600
Services Facilities--Installed - 39.6% of Installed Equipment Costs	410,400
Total Direct Plant Cost--	2,139,600
Indirect Costs	
Engineering and Supervision - 25.2% of Installed Equipment Costs	261,200
Construction Expense - 20.9% of Installed Equipment Costs	216,600
Total Direct and Indirect Costs	2,617,400
Contractor's Fee - 5% of Direct and Indirect Costs	130,900
Contingency - 10% of Direct and Indirect Costs	261,700
Fixed Capital Investment	3,010,000
Working Capital - 10% of Total Capital Investment	334,500
Total Capital Investment	$3,344,500

Manufacturing and Product Costs

Labor Requirements [16]--

Process 1-A--

	Operating Labor Men Required Per Shift
Extractor--1st Stage	1
Extractor--2nd Stage	1
Evaporator	1
Vacuum Evaporator	1
	4

$$4\text{ men}\left|\frac{3\text{ shifts}}{\text{day}}\right|\frac{8\text{ hr}}{\text{shift}}\left|\frac{\$7.00}{\text{hr}}\right|\frac{345\text{ day}}{\text{operating year}}\right| = \$231{,}840$$

Process 1-B--

Vacuum Evaporator	1
Extractor--1st Stage	1
Extractor--2nd Stage	1
Evaporator	1
Vacuum Evaporator	1
	5

$$5\text{ men}\left|\frac{3\text{ shifts}}{\text{day}}\right|\frac{8\text{ hr}}{\text{shift}}\left|\frac{\$7.00}{\text{hr}}\right|\frac{345\text{ day}}{\text{operating year}}\right| = \$289{,}800$$

Process 2-A--

Extractor	1
Separator	1/2
Evaporator	1
Vacuum Evaporator	1
	3 1/2

$$3\ 1/2\text{ men}\left|\frac{3\text{ shifts}}{\text{day}}\right|\frac{8\text{ hr}}{\text{shift}}\left|\frac{\$7.00}{\text{hr}}\right|\frac{345\text{ day}}{\text{operating year}}\right| = \$202{,}860$$

Process 2-B--

Vacuum Evaporator	1
Extractor	1
Separator	1/2
Evaporator	1
Vacuum Evaporator	1
	4 1/2

$$4\ 1/2\text{ men}\left|\frac{3\text{ shifts}}{\text{day}}\right|\frac{8\text{ hr}}{\text{shift}}\left|\frac{\$7.00}{\text{hr}}\right|\frac{345\text{ day}}{\text{operating year}}\right| = \$260{,}820$$

Raw Materials Cost [16]--

	Base	Gal/Year	$1/Year
Process 1-A--			
Pyrolytic Oil	.24/gal	7,100,000	1,704,000
MIBK	.34/#	111,700	253,800
	($2.272/gal)		1,957,800
Process 1-B--			
Pyrolytic Oil	.24/gal	7,100,000	1,704,000
MIBK	.34/#	77,400	175,800
	($2,272/gal)		1,879,800
Process 2-A--			
Pyrolytic Oil	.24/gal	7,100,000	1,704,000
MIBK	.34/#	112,900	256,500
	($2.272/gal)		1,960,500
Process 2-B--			
Pyrolytic Oil	.24/gal	7,100,000	1,704,000
MIBK	.34/#	67,900	154,300
	($2.272/gal)		1,858,300

Utility Summary--

Basis: 100% Capacity; 345 days/year

Steam--

	1-A	1-B	2-A	2-B
Demand (#/hr)	21,540	16,440	17,510	13,360
Cost $/#(1000)	2.30	2.30	2.30	2.30
Cost Per Year ($)	410,200	313,100	333,500	254,400

Cooling Water--

Gal/Hr	7,640	16,320	7,720	15,670
Gal/da	183,460	391,760	185,370	376,140
Cost: $/1000 gal	0.07	0.07	0.07	0.07
Cost/yr ($)	4,430	9,460	4,480	9,080

Electricity--Estimate 0.10 kwhr/# Product [16]

#/day product	228,700	215,200	198,700	190,700
kwhr/da	22,870	21,520	19,870	19,070
Cost $/kwhr	.042	.042	.042	.042
Cost/yr	331,386	311,825	287,916	276,324

Process 1-A--

Manufacturing Cost--

Raw Materials	1,957,800
Operating Labor	231,800
Operating Supervision + Clerical - 15% of Operating Labor	34,800
Utilities	
Steam	410,200
Cooling Water	4,400
Electricity	331,400
Maintenance and Repairs - 7% of Fixed Capital Investment/yr	229,000
Operating Supplies - 15% of Total Cost of M + R	34,300
Laboratory Charges - 15% of Operating Labor	34,800
Direct Production Costs	3,268,500
Fixed Charges - (Depreciation, Taxes, Insurance, Rent) - 10% of Total Product Cost	390,700
Plant Overhead Costs - 50% of (Operating Labor + Supervision + Maintenance)	247,800
Total Product Cost	3,907,000

Process 1-B--

Manufacturing Cost--

Raw Materials	1,879,800
Operating Labor	289,800
Operating Supervision + Clerical - 15% of Operating Labor	43,500
Utilities	
Steam	313,100
Cooling Water	9,500
Electricity	311,800
Maintenance and Repairs - 7% of Fixed Capital Investment/yr	238,300
Operating Supplies - 15% of Total Cost of M + R	35,700
Laboratory Charges - 15% of Operating Labor	43,500
Direct Production Costs	3,165,000
Fixed Charges - (Depreciation, Taxes, Insurance, Rent) - 10% of Total Product Cost	383,400
Plant Overhead Costs - 50% of (Operating Labor + Supervision + Maintenance)	285,800
Total Product Cost	3,834,200

Process 2-A--

Manufacturing Cost--

Raw Materials	1,960,500
Operating Labor	202,900
Operating Supervision + Clerical - 15% of Operating Labor	30,400
Utilities	
Steam	333,500
Cooling Water	4,500
Electricity	287,900
Maintenance and Repairs - 7% of Fixed Capital Investment/yr	208,500
Operating Supplies - 15% of Total Cost of M + R	31,300
Laboratory Charges - 15% of Operating Labor	30,400
Direct Production Costs	3,089,900
Fixed Charges - (Depreciation, Taxes, Insurance, Rent) - 10% of Total Product Cost	367,800
Plant Overhead Costs - 50% of (Operating Labor + Supervision + Maintenance)	220,900
Total Product Cost	3,678,600

Process 2-B--

Manufacturing Cost--

Raw Materials	1,858,300
Operating Labor	260,800
Operating Supervision + Clerical - 15% of Operating Labor	39,100
Utilities	
Steam	254,400
Cooling Water	9,100
Electricity	276,300
Maintenance and Repairs - 7% of Fixed Capital Investment/yr	210,700
Operating Supplies - 15% of Total Cost of M + R	31,600
Laboratory Charges - 15% of Operating Labor	39,100
Direct Production Costs	2,979,400
Fixed Charges - (Depreciation, Taxes, Insurance, Rent) - 10% of Total Product Cost	359,400
Plant Overhead Costs - 50% of (Operating Labor + Supervision + Maintenance	255,300
Total Product Cost	3,594,100

Depreciation

The depreciation over the 10 year life of the plant is shown for each of the four processes in TABLES 35 to 38. The tables give the annual and cumulative depreciation based on the double-declining balance method for the first five years with a switch to straight line depreciation for the remaining five years. The total depreciable amount includes (installed): equipment, instrumentation and controls, piping, electrical, buildings and services, yard improvements, service facilities and land. The total direct plant costs for each process are shown below:

Process 1A	$2,325,768
Process 1B	2,419,277
Process 2A	2,117,055
Process 2B	2,139,646

TABLE 35. DEPRECIATION - PROCESS 1A

End of Year	Annual	Cumulative
1	465,154	465,154
2	372,123	837,277
3	297,698	1,134,975
4	238,159	1,373,134
5	190,527	1,563,661
6	152,422	1,716,083
7	152,422	1,868,505
8	152,421	2,020,926
9	152,421	2,173,347
10	152,421	2,325,768

TABLE 36. DEPRECIATION - PROCESS 1B

End of Year	Annual	Cumulative
1	483,855	483,855
2	387,084	870,939
3	309,668	1,180,607
4	247,734	1,428,341
5	198,187	1,626,528
6	158,550	1,785,078
7	158,550	1,943,628
8	158,550	2,102,178
9	158,550	2,260,728
10	158,549	2,419,277

TABLE 37. DEPRECIATION - PROCESS 2A

End of Year	Annual	Cumulative
1	423,411	423,411
2	338,729	762,140
3	270,983	1,033,123
4	216,786	1,249,909
5	173,429	1,423,338
6	138,744	1,562,082
7	138,744	1,700,826
8	138,743	1,839,569
9	138,743	1,978,312
10	138,743	2,117,055

TABLE 38. DEPRECIATION - PROCESS 2B

End of Year	Annual	Cumulative
1	427,929	427,929
2	342,343	770,272
3	273,875	1,044,147
4	219,100	1,263,247
5	175,280	1,438,527
6	140,224	1,578,751
7	140,224	1,718,975
8	140,224	1,859,199
9	140,224	1,999,423
10	140,223	2,139,646

Products

The products generated by each of the four pyrolytic oil extraction processes are: Process 1A--insoluble oil, MIBK soluble organics and water soluble organics; Process 1B--volatiles, insoluble oil, MIBK soluble organics and water soluble organics; Process 2A, water soluble organics and MIBK soluble organics; and Process 2B, volatiles, water soluble organics and MIBK soluble organics. A survey of the prices of various chemicals was taken with the results listed in TABLE 39.

The volatiles contain about 68% water with about 20% acetic acid, by weight. The current market price of acetic acid is $0.23/lb. The selling price of the volatiles was estimated to be $0.23/lb of acetic acid contained in the fraction.

TABLE 39. PRICE SURVEY OF VARIOUS CHEMICALS [18]

Compound	Price	
	$/lb	$/gal
Benzene	.225	1.65
Cyclo Hexane	.279	1.75
Toluene	.17	1.25
Toluene (Coal Tar)	.19	1.35
Xylenes	.185	1.35
Ortho-Xylene	.22	
Para-Xylene	.28	
Meta-Xylene	.31	
Cumene	.15	
Napthalene	.25	
Styrene	.35	
Para-Tert-Amylphenol	.74	
Di-Tert-Amylphenol (85%)	.61	
Di-Tert-Amylphenol (95%)	.78	
Di-Tert-Amylphenol (97%)	.79	
Bis-Phenol-Polycarbonate Grade	.61	
Bis-Phenol-Epoxy Grade	.57	
Phenol (Synthetic)	.38	
Phenyl Acetate	1.04	
Acetophenone	.40	
Benzaldehyde	1.05-1.15	
Benzophenone	2.80-2.85	
Benzyl Alcohol	1.00-1.09	
Bisphenol-A Epoxy Grade	.47 - .52	
Diphenyl (99.9%)	.495	
O-Phenyl Phenol	1.35-2.00	
P-Phenyl Phenol	1.10-1.25	
Alcohol (Synthetic)-(C-12 to C-15)	.45	
Acetic Acid	.23	
Acetic Anhydride	.34	
Acetyldehyde	.265	
Acetone	.26	
MEK	.31	
Ethyl Amyl Ketone	.38	
MIBK	.34	
Mineral Spirits	.43	
Naptha (VM + P) (Varnish + Paint Makers)		.38
Tallow (Fatty Acids-Tech)	.32 - .49	
Tall Oil (Crude)	($150-160/ton)	
Napthol (Tech)	1.03	
Lacquer Diluent-Pet. Base	.38 - .40	

(continued)

TABLE 39 (continued)

Compound	Price		
	$/1b		$/gal
Epoxy Resin	.93		
Sucrose (#2)	.25		
Asphalt			.55-.65
Coal Tar Pitch	.085	($170/ton)	
Creosote-Coal Tar	.083		.83
Creosote (80/20 Solution)	.081		.81
M-Cresol (95-98%)	.98		
M,P-Cresol (90%)	.54		
M,P-Cresol (94%)	.55		
M,P-Cresol (97%)	.70		
O-Cresol (98%)	.55		
O-Cresol (99%)	.555		
P-Cresol (98%)	1.08		
Cresylic Acid-Coal Tar Der. (Resin Grade)	.54		
Molasses		($26/100#)	

The insoluble oil product is a heavy oil, somewhat similar to Bunker C. It was estimated to be comparable to coal tar pitch ($170 per ton or $0.085 per pound) or creosote - coal tar ($0.83 per gallon or $0.08 per pound). The insoluble oil fraction was given a selling price of $0.08 per pound in the minimum selling price case and a selling price of $0.09 per pound in the average and maximum selling price cases.

The uses of the water soluble organics and the MIBK soluble organics, the major products, have been discussed in detail. Some of the possible uses are, to review: a rubber oil additive, an epoxy intermediate, a resin feedstock, and an antioxidant additive for rubber. Prices of similar types of chemicals are: Styrene - $0.35/lb, Napthalene - $0.25/lb, Acetophenone - $0.40/lb, Bisphenol A Epoxy Grade - $0.47 to $0.52/lb, Cresylic Acid - $0.54/ lb, O-Cresol - $0.55/lb, M-Cresol - $0.98/lb, P-Cresol - $1.08/lb, and Mixed Cresols - $0.54 to $0.70/lb.

The estimated range of the selling price of the organics was $0.30 to $0.60/lb. These figures are based on the pounds of organics contained in a given quantity of product solution. Thus the water soluble organics and the MIBK soluble organics were given a selling price of $0.30/lb for the minimum selling price case, $0.50/lb for the average selling price case, and $0.60/lb for the maximum selling price case.

Sales Income

As shown in the products section, the main products, the MIBK soluble organics and the water soluble organics are estimated to have a selling price in the range of $0.30 per pound to $0.60 per pound. The average selling price, estimated by comparing the current market price of similar chemicals, is $0.50 per pound.

The sales income, in dollars per year, is shown below for 3 cases: minimum selling price ($0.30/lb), average selling price ($0.50/lb), and maximum selling price ($0.60/lb). The sales figures are based on a 24 hour per day operation, 345 day operating year at 100% capacity.

SALES INCOME--MINIMUM SELLING PRICE

Process 1-A--

	Basis	Quantity Produced	$/Yr
Insoluble Oil	0.08/lb	5049.6 lb/hr	3,344,860
MIBK Soluble Organics	0.30/lb	877.3 lb/hr	2,179,210
Water Soluble Organics	0.30/lb	3603.4 lb/hr	8,950,850
			$14,474,920

Process 1-B--

Volatiles	0.23/lb	269.1 lb/hr	512,470
Insoluble Oil	0.08/lb	5259.3 lb/hr	3,483,760
MIBK Soluble Organics	0.30/lb	565 lb/hr	1,403,460
Water Soluble Organics	0.30/lb	2873.8 lb/hr	7,138,530
			$12,538,220

Process 2-A--

	Basis	Quantity Produced	$/Yr
Water Soluble Organics	0.30/lb	6186.4 lb/hr	15,367,020
MIBK Soluble Organics	0.30/lb	2094 lb/hr	5,201,500
			$20,568,520

Process 2-B--

Volatiles	0.23/lb	269.1 lb/hr	512,470
Water Soluble Organics	0.30/lb	3954.2 lb/hr	9,822,230
MIBK Soluble Organics	0.30/lb	2722.8 lb/hr	6,763,440
			$16,585,670

SALES INCOME--AVERAGE SELLING PRICE

Process 1-A--

	Basis	Quantity Produced	$/Yr
Insoluble Oil	0.09/lb	5049.6 lb/hr	3,762,960
MIBK Soluble Organics	0.50/lb	877.3 lb/hr	3,632,020
Water Soluble Organics	0.50/lb	3603.4 lb/hr	14,918,080
			$22,313,060

Process 1-B--

Volatiles	0.23/lb	269.1 lb/hr	512,470
Insoluble Oil	0.09/lb	5259.3 lb/hr	3,919,230
MIBK Soluble Organics	0.50/lb	565 lb/hr	2,339,100
Water Soluble Organics	0.50/lb	2873.8 lb/hr	11,897,530
			$18,668,330

Process 2-A--

	Basis	Quantity Produced	$/Yr
Water Soluble Organics	0.50/lb	6186.4 lb/hr	25,611,700
MIBK Soluble Organics	0.50/lb	2094 lb/hr	8,669,160
			$34,280,860

Process 2-B--

Volatiles	0.23/lb	269.1 lb/hr	512,470
Water Soluble Organics	0.50/lb	3954.2 lb/hr	16,370,390
MIBK Soluble Organics	0.50/lb	2722.8 lb/hr	11,272,390
			28,155,250

SALES INCOME--MAXIMUM SELLING PRICE

Process 1-A--

	Basis	Quantity Produced	$/Yr
Insoluble Oil	0.09/lb	5049.6 lb/hr	3,762,960
MIBK Soluble Organics	0.60/lb	877.3 lb/hr	4,358,430
Water Soluble Organics	0.60/lb	3603.4 lb/hr	17,901,690
			$26,023,080

Process 1-B--

Volatiles	0.23/lb	269.1 lb/hr	512,470
Insoluble Oil	0.09/lb	5259.3 lb/hr	3,919,230
MIBK Soluble Organics	0.60/lb	565 lb/hr	2,806,920
Water Soluble Organics	0.60/lb	2873.8 lb/hr	14,277,040
			$21,515,660

Process 2-A--

	Basis	Quantity Produced	$/Yr
Water Soluble Organics	0.60/lb	6186.4 lb/hr	30,734,040
MIBK Soluble Organics	0.60/lb	2094 lb/hr	10,403,000
			$41,137,040

Process 2-B--

Volatiles	0.23/lb	269.1 lb/hr	512,470
Water Soluble Organics	0.60/lb	3954.2 lb/hr	19,644,470
MIBK Soluble Organics	0.60/lb	2722.8 lb/hr	13,526,870
			$33,683,810

RATE OF RETURN ANALYSIS

To obtain a rate of return discounted cash flow for the life of the plant, the following method was adopted: the plant life was assumed to be ten years beginning at year zero with the total initial investment spread over one year and ending at year zero.

Although an operating plant would be brought to full capacity gradually (i.e., 50% capacity 1st year, 75% capacity 2nd year, 100% capacity 3rd year on), for simplicity of calculation it was assumed that the plant would operate at 100% capacity over the 10-year period.

It was assumed that the initial investment was the sum of the fixed capital investment plus working capital. At the end of year 10, salvage was assumed to be zero, but the working capital would be recovered.

The depreciation schedules were calculated using the double-declining balance method for the first five years, switching to straight line depreciation for years 6-10.

Cash flows were calculated for each of the four processes before and after taxes, and are presented in TABLES 40 through 48. Taxes are 46% of gross profit. The average annual profit and return on investment (ROI) were calculated on an after tax basis.

For each process two cases were examined, in which annual sales income was varied. The change in annual sales income is based on the minimum selling price of $0.30 per pound and the average selling price of $0.50 per pound of the soluble organic products. The ROI for each of the cases is shown in TABLE 40 and expressed as a percent.

TABLE 40. RETURN ON INVESTMENT--SUMMARY

Process	Product Selling Price	
	$0.30/lb	$0.50/lb
1A	156.31%	272.74%
1B	123.60%	211.12%
2A	274.95%	498.72%
2B	209.10%	395.90%

TABLE 41. CASH FLOW--PROCESS 1-A--Case I--$0.30/1b

Year	Deprec.	Cumulative Cash Position Before Taxes	Gross Profit - Dep.	Taxes	Gross Profit - Taxes	Net Profit + Deprec.	Cash Position After Taxes
0		(3,635,416)					(3,635,416)
1	465,154	7,397,598	10,102,706	4,647,245	5,920,615	6,385,769	2,750,353
2	372,123	18,337,581	10,195,737	4,690,039	5,877,821	6,249,944	9,000,297
3	397,698	29,203,139	10,270,162	4,724,275	5,843,585	6,141,283	15,141,580
4	238,159	40,009,158	10,329,701	4,751,662	5,816,198	6,054,357	21,195,937
5	190,527	50,767,545	10,377,333	4,773,573	5,794,287	5,984,814	27,180,751
6	152,422	61,487,827	10,415,438	4,791,101	5,776,759	5,929,181	33,109,932
7	152,422	72,208,109	10,415,438	4,791,101	5,776,759	5,929,181	39,039,113
8	152,421	82,928,390	10,415,439	4,791,102	5,776,758	5,929,179	44,968,292
9	152,421	93,648,671	10,415,439	4,791,102	5,776,758	5,929,179	50,897,471
10	152,421	104,368,952	10,415,439	4,791,102	5,776,758	5,929,179	56,826,650

Fixed Capital Investment $3,271,874
Total Capital Investment $3,635,416

Sales (for each year) = $14,474,920
Manufacturing cost (for each year) = $3,907,060
Gross Profit (for each year) = $10,567,860

Average Annual Profit = $56,826,650/10 years = $5,682,665
ROI = $5,682,665/3,635,416 * 100% = 156.31%

TABLE 42. CASH FLOW--PROCESS 1-A--CASE II--$0.50/1b

Year	Deprec.	Cumulative Cash Position Before Taxes	Gross Profit-Dep.	Taxes	Gross Profit-Taxes	Net Profit + Deprec.	Cash Position After Taxes
0		(3,635,416)					(3,635,416)
1	465,154	15,235,738	17,940,846	8,252,789	10,153,211	10,618,365	6,982,949
2	372,123	34,013,861	18,033,877	8,295,583	10,110,417	10,482,540	17,465,488
3	297,698	52,717,559	18,108,302	8,329,819	10,076,181	10,373,879	27,839,368
4	238,159	71,361,718	18,167,841	8,357,207	10,048,793	10,286,952	38,126,320
5	190,527	89,958,245	18,215,473	8,379,118	10,026,882	10,217,409	48,343,729
6	152,422	108,516,667	18,253,578	8,396,646	10,009,354	10,161,776	58,505,505
7	152,422	127,075,089	18,253,578	8,396,646	10,009,354	10,161,776	68,667,281
8	152,421	145,633,510	18,253,579	8,396,646	10,009,354	10,161,775	78,829,056
9	152,421	164,191,931	18,253,579	8,396,646	10,009,354	10,161,775	88,990,831
10	152,421	182,750,352	18,253,579	8,396,646	10,009,354	10,161,775	99,152,605

Fixed Capital Investment $3,271,874
Total Capital Investment $3,635,416

Sales (for each year) = $22,313,060
Manufacturing cost (for each year) = $3,907,060
Gross Profit (for each year) = $18,406,000

Average Annual Profit = $99,152,605/10 years = $9,915,261
ROI = $9,915,261/3,635,416 * 100% = 272.74%

TABLE 43. CASH FLOW--PROCESS 1-B--CASE I--$0.30/lb

Year	Deprec.	Cumulative Cash Position Before Taxes	Gross Profit - Dep.	Taxes	Gross Profit - Taxes	Net Profit + Deprec.	Cash Position After Taxes
0		(3,782,363)					(3,782,363)
1	483,855	5,405,512	8,220,165	3,781,276	4,922,744	5,406,599	1,624,236
2	387,084	14,496,616	8,316,936	3,825,791	4,878,229	5,265,313	6,889,550
3	309,668	23,510,304	8,394,352	3,861,402	4,842,618	5,152,286	12,041,836
4	247,734	32,462,058	8,456,286	3,889,892	4,814,128	5,061,862	17,103,698
5	198,187	41,364,265	8,505,833	3,912,683	4,791,337	4,989,524	22,093,222
6	158,550	50,226,835	8,545,470	3,930,916	4,773,104	4,931,654	27,024,876
7	158,550	59,089,405	8,545,470	3,930,916	4,773,104	4,931,654	31,956,529
8	158,550	67,951,975	8,545,470	3,930,916	4,773,104	4,931,654	36,888,183
9	158,550	76,814,545	8,545,470	3,930,916	4,773,104	4,931,654	41,819,837
10	158,549	85,677,114	8,545,471	3,930,916	4,773,104	4,931,653	46,751,490

Fixed Capital Investment = $3,404,127
Total Capital Investment = $3,782,363

Sales (for each year)= $12,538,220
Manufacturing cost (for each year) = $3,834,200
Gross Profit (for each year) = $8,704,020

Average Annual Profit = $46,751,490/10 years = $4,675,149
ROI = $4,675,149/$3,782,363 * 100% = 123.60%

TABLE 44. CASH FLOW--PROCESS 1-B--CASE II--$0.50/1b

Year	Deprec.	Cumulative Cash Position Before Taxes	Gross Profit - Dep.	Taxes	Gross Profit - Taxes	Net Profit + Deprec.	Cash Position After Taxes
0		(3,782,363)					(3,782,363)
1	483,855	11,535,622	14,350,275	6,601,127	8,233,004	8,716,859	4,934,496
2	387,084	26,756,836	14,447,046	6,645,641	8,188,489	8,575,573	13,510,068
3	309,668	41,900,634	14,524,462	6,681,253	8,152,877	8,462,545	21,972,614
4	247,734	56,982,498	14,586,396	6,709,742	8,124,388	8,372,122	30,344,736
5	198,187	72,014,815	14,635,943	6,732,534	8,101,596	8,299,783	38,644,519
6	158,550	87,007,495	14,675,580	6,750,767	8,083,363	8,241,913	46,886,432
7	158,550	102,000,175	14,675,580	6,750,767	8,083,363	8,241,913	55,128,345
8	158,550	116,992,855	14,675,580	6,750,767	8,083,363	8,241,913	63,370,258
9	158,550	131,985,535	14,675,580	6,750,767	8,083,363	8,241,913	71,612,172
10	158,549	146,978,214	14,675,581	6,750,767	8,083,363	8,241,912	79,854,085

Fixed Capital Investment = $3,404,127
Total Capital Investment = $3,782,363

Sales (for each year) = $18,668,330
Manufacturing cost (for each year) =$3,834,200
Gross Profit (for each year) = $14,834,130

Average Annual Profit = $79,854,085/10 years = $7,985,409
ROI = $7,985,409/$3,782,363 * 100% = 211.12%

TABLE 45. CASH FLOW-PROCESS 2-A--CASE I--$0.30/1b

Year	Deprec.	Cumulative Cash Position Before Taxes	Gross Profit - Dep.	Taxes	Gross Profit - Taxes	Net Profit + Deprec.	Cash Position After Taxes
0		(3,309,177)					(3,309,177)
1	423,411	14,004,134	16,466,489	7,574,585	9,315,315	9,738,726	6,429,549
2	338,729	31,232,763	16,551,171	7,613,539	9,276,361	9,615,090	16,044,639
3	270,983	48,393,646	16,618,917	7,644,702	9,245,198	9,516,181	25,560,821
4	216,786	65,500,332	16,673,114	7,669,632	9,220,268	9,437,054	34,997,874
5	173,429	82,563,661	16,716,471	7,689,577	9,200,323	9,373,752	44,371,626
6	138,744	99,592,305	16,751,156	7,705,532	9,184,368	9,323,112	53,694,739
7	138,744	116,620,949	16,751,156	7,705,532	9,184,368	9,323,112	63,017,851
8	138,743	133,649,592	16,751,157	7,705,532	9,184,368	9,323,111	72,340,962
9	138,743	150,678,235	16,751,157	7,705,532	9,184,368	9,323,111	81,664,073
10	138,743	167,706,878	16,751,157	7,705,532	9,184,368	9,323,111	90,987,185

Fixed Capital Investment = $2,978,259
Total Capital Investment = $3,309,177

Sales (for each year) = $20,568,520
Manufacturing cost (for each year) = $3,678,620
Gross Profit (for each year) = $16,889,900

Average Annual Profit = $90,987,185/10 years = $9,098,719
ROI = $9,098,719/$3,309,177 * 100% = 274.95%

TABLE 46. CASH FLOW--PROCESS 2-A--CASE II--$0.50/lb

Year	Deprec.	Cumulative Cash Position Before Taxes	Gross Profit - Dep.	Taxes	Gross Profit - Taxes	Net Profit + Deprec.	Cash Position After Taxes
0		(3,309,177)					(3,309,177)
1	423,411	27,716,474	30,178,829	13,882,261	16,719,979	17,143,390	13,834,213
2	338,729	58,657,443	30,263,511	13,921,215	16,681,025	17,019,754	30,853,967
3	270,983	89,530,666	30,331,257	13,952,378	16,649,862	16,920,845	47,774,811
4	216,786	120,349,692	30,385,454	13,977,309	16,624,931	16,841,717	64,616,529
5	173,429	151,125,361	30,428,811	13,997,253	16,604,987	16,778,416	81,394,944
6	138,744	181,866,345	30,463,496	14,013,208	16,589,032	16,727,776	98,122,720
7	138,744	212,607,329	30,463,496	14,013,208	16,589,032	16,727,776	114,850,496
8	138,743	243,348,312	30,463,497	14,013,208	16,589,032	16,727,775	131,578,271
9	138,743	274,089,295	30,463,497	14,013,208	16,589,032	16,727,775	148,306,046
10	138,743	304,830,278	30,463,497	14,013,208	16,589,032	16,727,775	165,033,821

Fixed Capital Investment = $2,978,259
Total Capital Investment = $3,309,177

Sales (for each year) = $34,280,860
Manufacturing cost (for each year) = $3,678,620
Gross Profit (for each year) = $30,602,240

Average Annual Profit = $165,033,821/10 years = $16,503,382
ROI = $16,503,382/$3,309,177 * 100% = $498,72%

TABLE 47. CASH FLOW--PROCESS 2-B--CASE I--$0.30/1b

Year	Deprec.	Cumulative Cash Position Before Taxes	Gross Profit - Dep.	Taxes	Gross Profit - Taxes	Net Profit + Deprec.	Cash Position After Taxes
0		(3,344,489)					(3,344,489)
1	427,929	10,074,940	12,563,571	5,779,243	7,212,257	7,640,186	4,295,697
2	342,343	23,408,783	12,649,157	5,818,612	7,172,888	7,515,231	11,810,928
3	273,875	36,674,158	12,717,625	5,850,108	7,141,393	7,415,268	19,226,196
4	219,100	49,884,758	12,772,400	5,875,304	7,116,196	7,335,296	26,561,492
5	175,280	63,051,538	12,816,220	5,895,461	7,096,039	7,271,319	33,832,810
6	140,224	76,183,262	12,851,276	5,911,587	7,079,913	7,220,137	41,052,947
7	140,224	89,314,986	12,851,276	5,911,587	7,079,913	7,220,137	48,273,085
8	140,224	102,446,710	12,851,276	5,911,587	7.079,913	7,220,137	55,493,222
9	140,224	115,578,434	12,851,276	5,911,587	7.079,913	7,220,137	62,713,359
10	140,223	128,710,157	12,851,277	5,911,587	7.079,913	7,220,136	69,933,495

Fixed Capital Investment = $3,010,040
Total Capital Investment = $3,344,489

Sales (for each year) = $16,585,670
Manufacturing cost (for each year) = $3,594,170
Gross Profit (for each year) = $12,991,500

Average Annual Profit = $69,933,495/10 years = $6,993,350
ROI = $6,993,350/$3,344,489 * 100% = 209.10%

TABLE 48. CASH FLOW--PROCESS 2-B--CASE II--$0.50/1b

Year	Deprec.	Cumulative Cash Position Before Taxes	Gross Profit - Dep.	Taxes	Gross Profit - Taxes	Net Profit + Deprec.	Cash Position After Taxes
0		(3,344,489)					(3,344,489)
1	427,929	21,644,520	24,133,151	11,101,249	13,459,831	13,887,760	10,543,271
2	342,343	46,547,943	24,218,737	11,140,619	13,420,461	13,762,804	24,306,075
3	273,875	71,382,898	24,287,205	11,172,114	13,388,966	13,662,841	37,968,916
4	219,100	96,163,078	24,341,980	11,197,311	13,363,769	13,582,869	51,551,785
5	175,280	120,899,438	24,385,800	11,217,468	13,343,612	13,518,892	65,070,677
6	140,224	145,600,742	24,420,856	11,233,594	13,327,486	13,467,710	78,538,387
7	140,224	170,302,046	24,420,856	11,233,594	13,327,486	13,467,710	92,006,097
8	140,224	195,003,350	24,420,856	11,233,594	13,327,486	13,467,710	105,473,807
9	140,224	219,704,654	24,420,856	11,233,594	13,327,486	13,467,710	118,941,518
10	140,223	244,405,958	24,420,857	11,233,594	13,327,486	13,467,709	132,409,927

Fixed Capital Investment = $3,010,040
Total Capital Investment = $3,344,489

Sales (for each year) = $28,155,250
Manufacturing cost (for each year) = $3,594,170
Gross Profit (for each year) = $24,561,080

Average Annual Profit = $132,409,927/10 years = $13,240,993
ROI = $13,240,993/$3,344,489 * 100% = 395.90%

Since the ROI for each case presented in TABLE 40 is extremely high, and not normally encountered in practice, a second method was adopted to determine the profitability of the pyrolytic oil separation processes. Using all the assumptions previously stated, three rates of return were selected - 15%, 30%, and 50%, and the selling price of the products necessary to produce this ROI was calculated. For this analysis the product streams were totaled and all products were assumed to have the same selling price per pound. The results are presented in TABLE 49. The rates of return are on an after tax basis. The required average selling price per pound of product varies from $0.0543 per pound to $0.1063 per pound. This corresponds to a raw pyrolytic oil cost (feedstock) of $0.24 per gallon, based on $2.30 per MM BTU, or $0.023 per pound.

TABLE 49. MINIMUM SELLING PRICE PER POUND TO JUSTIFY INVESTMENT

Process	Average Annual Profit Required	Price Per Pound of Product to Generate the Given ROI 15%	30%	50%	Total Product 10^6 lb/yr
1A	$ 545,300	0.0543			78.91
	1,090,600		0.0671		
	1,817,700			0.0842	
1B	567,400	0.0569			74.23
	1,134,700		0.0711		
	1,891,200			0.0899	
2A	496,400	0.0587			68.56
	992,800		0.0721		
	1,654,600			0.0899	
2B	501,700	0.0686			57.51
	1,003,300		0.0847		
	1,672,200			0.1063	

SECTION 8

DISCUSSION

PYROLYSIS OF LIGNOCELLULOSIC MATERIALS AND PROPERTIES OF THE OILS

The pyrolysis of lignocellulosic and similar materials produces char, organic substances, water and gases. Condensation of the off-gas stream from the pyrolysis will yield an organic phase and an aqueous phase. Pyrolysis of pine sawdust on a batch basis and the products has been described in detail [11]. The oils produced from pyrolytic processes were the focus of this investigation with the emphasis on characterization and maximum resource recovery by processing to produce more useful fractions for chemical applications.

Pyrolytic oils contain a wide spectrum of organic compounds, both aromatic and aliphatic. Most of these compounds are oxygenated, and consequently, the oils contain many functional groups. The oils must be considered therefore as a chemical feedstock and as a source of chemical materials for industrial applications. In order to develop the potential of pyrolytic oils as a chemical feedstock, characterization of chemical and physical properties of the pyrolytic oils is absolutely necessary. The data from the characterization of the oils can then be used in the development of processes for the oils to yield fractions that have chemical applications or that can be further refined or processed to yield useful chemical products.

The production of pyrolytic oils is an important and significant factor in the overall utilization of these oils. Some of the factors that affect the quality and characteristics of the oils are feed materials, pyrolysis mode (vertical bed reactor, flash pyrolysis, fluidized bed reactor, etc.), pyrolysis conditions (temperature, presence or absence of air, feed material size, etc.) and recovery mode from the off-gas stream. For this investigation, the oils were obtained from the Tech-Air Corporation's 50 dry ton/day pyrolysis facility and the pyrolysis pilot plants on the Georgia Tech campus which utilize the Georgia Tech process [6, 7]. Oils obtained from pilot plants and field demonstration units which operate on a continuous basis at steady state conditions are representative of the oils that would be produced on a commercial scale. Therefore, the results and data obtained from a study with these oils will be more applicable in the processing and recovery of useful products from commercially produced pyrolytic oils.

Pyrolytic oils from the Tech-Air 50 dry ton/day facility have been thoroughly characterized as to overall general properties such as heating value, elemental content, acidity, etc., and these results have been reported

[12]. In general, the oils are dark brown to black and have a pungent, burnt odor. The viscosity of the oils will depend upon the amount of water present in the oils. The water is well emulsified and does not separate on standing. With a water content of 25% or greater the oils are relatively thin and free flowing. Oils which are essentially free of water are viscous, and some have a grease-like consistency at ambient temperature. The viscosity decreases with temperature for short periods of heating. The oils are heat sensitive and prolonged heating will result in increasing viscosity with eventual formation of solids. The oils are combustible and can be burned very satisfactorily with the proper burner. Burning tests of the oils admixed with fuel oil and with char have been very satisfactory. The oils are acidic and exhibit corrosive properties. This characteristic must be taken into account in the storage and processing of the oils.

ANALYSIS AND CHARACTERIZATION OF PYROLYTIC OILS

The pyrolytic oils are a complex mixture of organic compounds with a wide range in boiling point from highly volatile substances to very high boiling substances. The oils contain oxygen in the range of 20 to 40 percent, and therefore, there is a large number of oxygen containing compounds present which have a variety of organic functional groups such as carbonyl, hydroxyl, ether, etc. The oils are heat sensitive and begin to decompose at 175° to 200°C. The chemical and physical analysis of pyrolytic oils therefore is not a simple task. It is very difficult to analyze the oils, or fractions obtained from the oils, for chemical content as to classes of organic compounds and as to functionality. This aspect of this project has been very difficult, and there is a need for additional work in the chemical analysis of pyrolytic oils.

For overall properties of pyrolytic oils, many of the ASTM methods are applicable to pyrolytic oils. The tests used in characterizing and analyzing pyrolytic oils from the Tech-Air Cordele development unit are given in TABLE 2. The distillation test, ASTMD-86, is not too useful as most of the oils start to decompose at the point when approximately 50 to 60 percent of the oil has distilled. The development of more meaningful tests will be necessary as pyrolytic oils find greater utility as fuels.

The chemical composition of the pyrolytic oils are of importance and significance in developing processing methods for the oils. A knowledge of the components in the oils will serve as guidelines for devising processing methods for separation of the oils into fractions containing a major chemical class of substances, i.e., phenolics. The oils are chemically complex and contain a wide variety of aliphatic, aromatic and heterocyclic compounds. The analytical techniques that are very useful and valuable in determining the composition of the oils are liquid chromatography (LC), gas chromatography (GC), thin layer chromatography (TLC), gas chromatography/mass spectroscopy (GC/MS), and infrared spectroscopy.

Considerable effort was placed on both liquid and gas chromatography in this investigation and both were used extensively in this work with the oils. LC is an excellent analytical technique for these oils as it is carried out at ambient temperature, is capable of high resolution of complex organic mixtures and component detection is nondestructive. The oils are heat sensitive, and hence, LC is particularly useful with these oils. In addition, the pyrolytic oils are soluble in organic-water solvent systems which are very useful in LC. A variety of LC columns and conditions were tested in determining suitable conditions for analyzing pyrolytic oils. Particular interest was in using LC as a "finger-printing" method for the oils and fractions obtained from them by various processing techniques. A Partisil ODS 5µ column with a water-acetonitrile solvent system and a flow rate of one ml per minute was found to produce very satisfactory chromatograms. In Phase III of the experimental work, the column used for LC was a 25 cm Spherosal ODS C_{18} column. The most useful ultraviolet detector settings are 280 nm and 254 nm for our purposes. LC was used throughout this investigation for the "finger-printing" of the oils and fractions of the oils obtaining by different processing methods.

Gas chromatography (GC) offers an excellent technique for analyzing complex mixture of organic compounds. The disadvantage with GC with pyrolytic oils is the heat sensitivity of the oils since GC analysis involves temperatures up to 250°C for these oils. Recognizing this as a possible constraint, GC should be useful for analysis of fractions containing more volatile components, of water soluble components and of fractions obtained in experiments designed to separate the raw oils into fractions containing a major chemical class of compounds. A variety of column packings and conditions were tested. A column containing 10% methylsilicone fluid has been found to be very useful with the raw oils and fractions with higher boiling components, and a column containing 10% Carbowax 20M has been found satisfactory for low boiling components. In Phase III of the experimental work, a Pora Pak Q column was used for water and water soluble organics.

Thin layer chromatography was utilized in Phase III of the experimental program as it offered a very rapid and useful technique for analyzing the different phases and fractions obtained in the extraction experiments. Details are given in Phase III of the experimental section.

A nonaqueous titration method was devised and used to determine the presence of phenolics in the oils and fractions obtained from the oils by the various extraction techniques. The technique has utility with these oils so long as the limitations are recognized. More details are given in the experimental section, Phase III.

In our attempts to analyze the pyrolytic oils, and particularly the fractions obtained from the oils by the various processing techniques, the data from LC, TLC, IR, GC and nonaqueous titration were used and evaluated. The most promising avenues for improving the chemical analytical data with the fractions obtained from the oils are to correlate the components obtained in GC, LC and TLC with GC/MS and IR data. For pilot work with pyrolytic oils, there is a need for rapid analytical techniques to follow the process during actual operation. TLC may offer a potential method for this need.

DISTILLATION

The distillation of complex liquids is a widely used process that has reached a high degree of sophistication in the chemical industry. Therefore, distillation offers a possible method for processing and refining pyrolytic oils. It is particularly useful for obtaining fractions with fairly close boiling range. A number of distillation experiments were conducted with the raw oils. These included distillation at atmospheric pressure, and at 0.2 - 0.4 mm mercury, fractional distillation at reduced pressure, steam distillation and vacuum stripping.

The distillation of the raw oils at both atmospheric and low pressures would yield from 55 to 65 percent distillate. The charge in the flask would become more viscous as the distillation proceeded, and when 55 to 65 percent had distilled, the remaining oil in the flask would begin to decompose and smoke. In some cases, the charge would decompose quickly with an evolution of gases. From these experiments, it was concluded that distillation of the raw oils was not a suitable first step for processing the oils.

The distillate from a simple vacuum distillation of raw pyrolytic oil was fractionated at approximately 2 mm pressure. The distillation did not yield any fractions with a close boiling range. The liquid chromatograms of the fractions indicated, however, that the more polar and water soluble components were concentrated in the low boiling fractions whereas the less polar components were concentrated in the higher boiling fractions. A sample of water-insoluble oil, which had been prepared by the water extraction of vacuum stripped oil, was distilled at approximately 6 mm pressure. Approximately, 47 percent of the sample distilled from 50°C up to 193°C, and no close-boiling fractions were obtained. Analysis of the five fractions by TLC, LC, and IR indicated that the first four fractions, approximately 29 percent of the charge, contained mainly phenolic aromatics and phenolic ethers. The chemical analyses indicated that fraction 5, boiling point range 175° - 193°C and approximately 17 percent of the charge, contained mainly phenolic ethers and aromatic neutrals with a trace of polyhydroxy neutral compounds. The results with the distillation of fractions obtained from raw pyrolytic oil samples show that distillation of oil fractions produced from raw oil by other separation techniques can be used to yield more highly refined chemical materials.

Steam distillation of pyrolytic oil samples showed that a relatively small amount of the oils were steam distilled. The steam distillate contained more polar and water soluble components of the oil. The liquid chromatogram of the steam distillate was very similar to the liquid chromatograms of the water extracts at 25°C, 50°C and 95°C of the oil, indicating that steam distillation and water extraction of the oils produced very similar fractions of the oils. These results indicate that steam distillation is not a suitable processing step for the raw oils. Vacuum stripping of the oils at ambient temperature was found to be an effective way to remove the water and some of the volatile organics, which included the acids.

HYDROGENATION

Hydrogenation was considered as a possible means of improving the processing characteristics of the oils. A series of hydrogenation experiments with raw pyrolytic oil samples were carried out at 4 atmospheres and 20 atmospheres. The Pd catalyst performed better than the Pt catalyst. The amount of hydrogen absorbed was in the range of 2 mg/g of oil from pine wood and 3 to 5 mg/g of oil from hardwood. If one assumes an average molecular weight of 150 for the oil, then approximately 0.15 mole of hydrogen is absorbed per mole of oil for 2 mg of hydrogen absorbed/g of oil. These preliminary experiments at relative low pressure indicated that hydrogenation should not be considered as an initial step in processing pyrolytic oils. Additional hydrogenation experiments should be conducted with fractions of oil obtained by various separation techniques including some at higher pressures than used in this work.

EXTRACTION EXPERIMENTS

Some factors that are important and must be considered in developing processing technology to produce fractions of pyrolytic oil that are suitable for chemical applications are the wide spectrum of organic compounds present in the oils, the quantity of each compound is relatively low, the oils are heat sensitive and chemically reactive, the solubility characteristics of the oils, and the volatiles (boiling point 100°C or less) including water in the raw oils. Two chemical operations that seemed most appropriate to investigate as processing steps were distillation and extraction. Distillation has been discussed above, and based on our results fractional distillation at reduced pressure on oil fractions obtained by an extraction process should be seriously considered as an operation to yield highly refined products. The focus of the processing study and the major effort was with extraction methods. The study initially was based on bench scale experiments with five different approaches. Based on the results of these experiments, three processes were selected for further investigation with batch processing. For the continuous extraction experiments, two processes were selected from the batch processing studies for investigation with both raw pyrolytic oil and vacuum stripped oil.

Bench Scale Extraction Experiments

Five major approaches involving extraction techniques were tested at the bench level. These approaches, which are discussed in the experimental section with results, were as follows:

A - Extraction of oil sequentially with water at 25°C, 50°C and 95°C.
B - Extraction of oil with sodium sulfate solution (salting out effect).
C - Extraction of oil simultaneously with an organic solvent and water (three phase system).
D - Extraction of sodium hydroxide solution at different pH ranges with methylene chloride.
E - Extraction of organic solvent solutions of pyrolytic oil with water.

Each of these approaches, or combinations, offer possibilities that can be utilized in a final process that will result in the production of fractions of oil for chemical applications. Based on some initial results with both raw and vacuum stripped oil, it was decided to use vacuum stripped oil in these batch experiments at the bench level. Treatment of the raw oil at reduced pressure and ambient temperature removes volatiles (largely acidic) and most of the water. The significant results for each approach are presented.

From process A, approximately 50% of the original raw oil was isolated as a water insoluble organic fraction, which contained about 20% phenolics and 80% aromatic neutrals. The separation of this fraction into the two major compound classes is very desirable. Subsequent processing techniques that are potentially useful are fractional distillation and other extraction steps. The three aqueous fractions, if combined, would contain approximately 34% of the original oil with 27% phenolics and 73% polyhydroxy neutral substances. A potential means for separation of these two chemical classes is the use of the salting-out technique which is the basis of process B. The advantage of process A is that water is a cheap solvent and nonhazardous, and the process should be relatively simple.

Process B, which involves essentially a salting out effect with sodium sulfate, offers a possibility for separation of the polyhydroxy neutral substances. The first step would be as depicted in Figure 28. The aqueous fraction contained organics with approximately 70% phenolics. This separation could possibly be improved by determining optimum conditions. The insoluble fraction could be extracted with water to remove the polyhydroxy neutral substances leaving an insoluble oil fraction. The salting out technique has the disadvantages of the organics having to be recovered from the concentrated salt solution and of the recovery and recycling the salt solution.

Process C, the three phase system, offers some interesting separation possibilities. It should be noted that the phenolics in the oil are separated about 50-50 in processes A and B and in process C, Figure 29, the aqueous phase contains about 50% of the phenolics and the remaining 50% is about evenly divided between the ether phase and the insoluble oil phase. Fractional distillation of the separate oil and ether fractions should yield fractions with high concentration of phenolics and the aromatic neutrals. The three phase approach with anisole produced results as shown in Figure 30. The quantities of the components in the aqueous fraction are about the same as when diisopropyl ether was used. The anisole, however, dissolves a much greater portion of the oil than diisopropyl ether.

In process D, two percent sodium hydroxide solution was used as a solvent for the oil followed by extraction with methylene chloride at three different pH ranges, 8 to 10, 5 to 7, and 1 to 3. Approximately, 53% of the oil charge dissolved in 300 ml of 2% NaOH. The extraction with CH_2Cl_2 at pH 8 to 10 gave predominantly aromatic neutrals whereas at the low pH range, the extract contained predominantly phenolics. Approximately 55% of the phenolics were in the aqueous phase with the remainder distributed in the three CH_2Cl_2 extracts. The remainder of the charge dissolved in 400 ml of 2% NaOH, and the solution was extracted in the same manner as above. It should be noted that in the first CH_2Cl_2 extract, approximately 92% of the organics was aromatic neutral compounds. Also, in the aqueous phase, approximately 58% of the organics was phenolics. Additional bench scale work is needed with this process to determine its usefulness as a method of processing pyrolysis oil. This approach has the disadvantages that it involves a number of processing steps and no one extraction produced a clear fraction of a given class of compounds present in the pyrolytic oil.

In process E, the organic solvents tested were methylene chloride and n-butanol. Two solutions of pyrolysis oil in methylene chloride were extracted with water followed by extraction of the aqueous solution in one experiment with diisopropyl ether and in the second experiment with methyl isobutyl ketone (MIBK). The results are shown schematically for the two experiments in Figures 32 and 33, respectively. A significant result of these two experiments is that the polyhydroxy neutral substances are concentrated in the aqueous phase along with 50 to 60% of the phenolics in the oil. The methylene chloride fraction contains phenolics and aromatic neutral compounds which could be fractional distilled to provide more desirable and useful fractions of the oil. Another approach to the treatment of the aqueous fraction is extraction with MIBK. The extraction of the aqueous fraction with MIBK gave a solution with approximately 92% phenolics, which represents approximately 35% of the phenolics in the aqueous fraction.

A solution of pyrolysis oil in n-butanol was extracted with water to determine the separation that would be obtained and the results are shown schematically in Figure 34. The polyhydroxy neutral substances are distributed between the aqueous fraction and the n-butanol fraction which is not a desirable result. Consequently, this approach was not pursued.

An examination of the data from the process approaches discussed above shows that for each approach approximately 50% of the phenolic content of the oil is in the aqueous fraction with the remainder in the insoluble oil phase or in the organic solvent phase. This could be of significance in that each of these phenolic fractions could have greater utility for specific uses than a single combined fraction of the phenolics. The aqueous fractions from all of the approaches contain relatively large amounts of polyhydroxy neutral substances with the exception of the salting out techniques.

The aqueous insoluble fractions contain approximately 50% of the phenolic content of the oil along with most of the aromatic neutral compounds with ratios of phenolics to aromatic neutral compounds in the range of 1 to 3 and 1 to 4. The separation of this fraction into the two major classes of compounds could possibly be accomplished by fractional distillation or extraction with an alkaline solution.

Careful examination of the data from the bench scale experiments with the five processes and consideration of each overall process as a continuous chemical process indicated that processes A and C are the most promising with process E offering some potential.

Continuous Extraction Experiments

The extraction experiments and related work for this phase of the program is described in the Experimental Section, Phase III. The pyrolytic oil used in these experiments was produced in the Georgia Tech pyrolysis pilot plant under carefully controlled conditions in October, 1978, from pine chips.

Based on the results from the bench scale extraction experiments described above, the decision was made to investigate further the three extraction methods, listed below, with both raw and vacuum stripped pyrolytic oil.

- •Process No. 1 - Water Extraction
- •Process No. 2 - Simultaneous Extraction with Water and an Organic Solvent
- •Process No. 3 - Dissolution in an Organic Solvent Followed by Water Extraction

Additional batch experiments were conducted with 100, 200 or 500 g oil samples using the three approaches. The results with Process No. 1 in this phase were comparable to the results in Experimental Phase II with aqueous extraction. The results indicate that MIBK is a better solvent than chloroform for extraction of the aqueous phase. Based on the results and observations of the experiments with Process No. 2, MIBK was selected as the solvent for the continuous extraction experiments. Also, in these batch experiments with the three phase system, the insoluble tar phase was very small, 2 percent or less, whereas in the initial experiments with the three phase process using diisopropyl ether, the insoluble phase was 25 percent. With Process No. 3, an insoluble tar phase was present in each experiment. It was decided to discontinue experimentation with this approach as it did not appear to offer any advantage over the simultaneous use of water and an organic solvent, Process No. 2.

The continuous countercurrent experiments were conducted with Process No. 1 and Process No. 2 with both raw and vacuum stripped pyrolytic oil. Some important observations from the results of the continuous extraction experiments are that the polyhydroxy neutrals are essentially concentrated in the aqueous phases for all four experiments, that the aromatic neutrals in the aqueous phase are extracted essentially completely into the MIBK fraction along with some phenolics and that the insoluble oil phases of Process No. 1 and the MIBK phases of Process No. 2 contain phenolics and aromatic neutrals. The MIBK phases and fractions and the insoluble oil phases which contain mainly phenolics and aromatic neutrals could be further processed by fractional distillation. Concentration of the extracted aqueous fractions, which contain phenolics (approximately 15 to 30 percent) and polyhydroxy neutrals, from both processes could yield a solution from which additional phenolics could be extracted. The results of these experiments are very promising that pyrolytic oils can be processed by extraction techniques to yield fractions that have potential for chemical applications or that can be refined through additional chemical processing operations.

PILOT PLANT

Based on the data obtained from the continuous countercurrent extraction experiments at the bench level, a versatile pilot plant was designed which can be used to test the water extraction Process No. 1 and the simultaneous extraction Process No. 2 with water and an organic solvent. The processes can be tested with both raw oil and vacuum stripped oil at a rate of four gallons per minute. In addition to the various extraction operations, oil fractions could be further processed by distillation. The data from the continuous extraction experiments indicate that the extraction approach is a very promising one by which fractions of the oil can be obtained which can be processed by additional operations, particularly fractional distillation, to yield products of greater utility. With a pilot plant, the concept can be demonstrated and sufficient quantities of oil fractions can be obtained for testing and development for industrial applications. More details on the pilot plant and schematics are given in Section 6.

ECONOMICS

In order to make some preliminary economic assessments for processing pyrolytic oils into materials for chemical applications, it was necessary to base the analysis on the data from the bench scale countercurrent continuous extraction experiments with the two processing modes with raw and vacuum stripped oils. The major assumptions were that pyrolytic oils, either raw or vacuum stripped, could be processed on a continuous basis by the two processing modes and that the processing modes would yield oil fractions which would be suitable for commercial applications. The major objective of this analysis was to determine if the processing of pyrolytic oils appeared to be economically feasible.

It was assumed the pyrolytic oil plant would process oil produced by five wood pyrolysis plants, each processing five dry tons per hour for 345 days per year. The yield of oil was assumed to be 18 percent on a dry weight basis, which amounts to approximately 7,100,000 gallons per year. The oil was assumed to have a heating value of 10,000 Btu/lb and a density of 10 lb per gallon. The cost of the oil to the plant was based on a value of $2.30 per million Btu.

The analysis was approached in two ways. In one method, the average selling price per pound for the total output from each process mode was determined to provide a net return on investment (ROI) for 15, 30, and 50 percent. The average selling price per pound for each process for this approach is given in TABLE 50. The significance of this analysis is that it shows that the selling price -- 8.4 to 10.6 cents per pound -- for the oil fractions for a 50 percent return on investment is in the range of quoted market prices in December, 1979, for similar materials, such as coal tar creosote at 9 cents per pound and well below the quoted prices for coal tar cresylic acid at 54 cents per pound. In the other method, the analysis was made on the basis that for case one, the oil product selling prices would be 8 cents per pound for the insoluble oil, 23 cents per pound for the organic volatiles from the oil stripping and 30 cents per pound for both the MIBK soluble and water soluble organics. In case two, the insoluble oil was 9 cents per pound, the organic volatile fraction, 23 cents per pound and both the MIBK soluble and water soluble organics, 50 cents per pound. The return on investment for each case is presented in TABLE 51. Each specific process for each case provides an

TABLE 50. AVERAGE SELLING PRICE FOR PYROLYTIC OIL PRODUCTS

	Net Return on Investment		
Process	15%	30%	50%
1A	5.4¢/lb	6.7¢/lb	8.4¢/lb
1B	5.7¢/lb	7.1¢/lb	9.0¢/lb
2A	5.9¢/lb	7.2¢/lb	8.4¢/lb
2B	6.9¢/lb	8.4¢/lb	10.6¢/lb

TABLE 51. RETURN ON INVESTMENT - PERCENT

Process	Case 1	Case 2
1A	156	273
1B	124	211
2A	275	499
2B	209	396

excellent return on investment. The significance of these results is that the economic feasibility appears to be very promising for processing the oil into products for commercialization. In order to realize the potential for processing pyrolytic oil into chemical materials on a commercial scale, it would be necessary to study and obtain more data by processing pyrolytic oils with a small scale pilot plant (see Section 6) and to investigate commercial applications for oil fractions produced with the pilot plant. In this way, reliable operating costs could be established and commercial value of the products could be determined.

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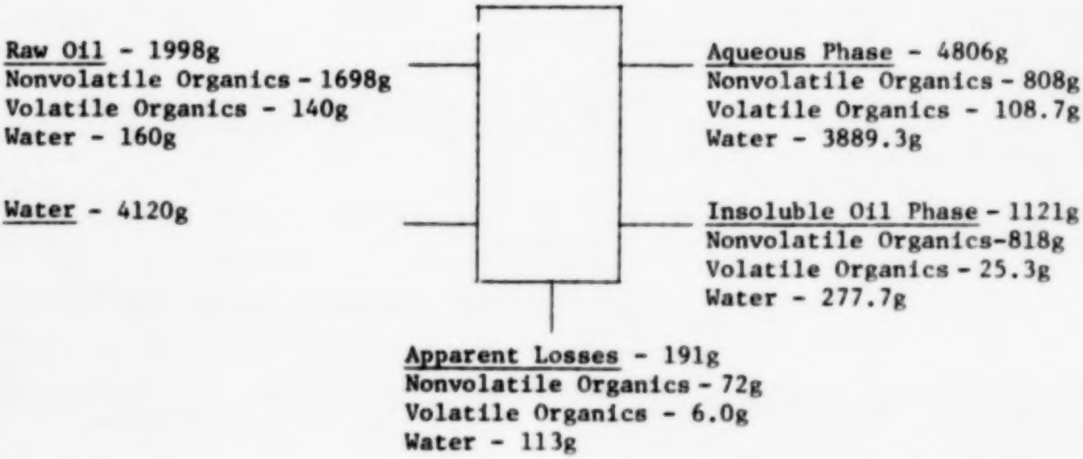
APPENDIX A

MATERIAL BALANCE CALCULATIONS

LABORATORY SCALE--CONTINUOUS EXTRACTION

Process 1-A--Raw Oil-Two Stage Extraction--Total Reactant and Product Balance

Extractor--1st Stage



Raw Oil - 1998g
Nonvolatile Organics - 1698g
Volatile Organics - 140g
Water - 160g

Water - 4120g

Aqueous Phase - 4806g
Nonvolatile Organics - 808g
Volatile Organics - 108.7g
Water - 3889.3g

Insoluble Oil Phase - 1121g
Nonvolatile Organics-818g
Volatile Organics - 25.3g
Water - 277.7g

Apparent Losses - 191g
Nonvolatile Organics - 72g
Volatile Organics - 6.0g
Water - 113g

TABLE A-1. FLOWRATES--RUN NO. 1-A

HP-29C--Linear Curve Fit*

The data is fitted to a straight line (linear regression). The form of the equation is shown below, with x = time, (min.), y = accumulated stream input or output (grams).

$$y = a + bx$$

Raw Oil Input Rate	$a = 10.949$
$n = 21$	$b = 10.5964$ grams/min
	$r^2 = 0.99732$
Water Input Rate	$a = 8.0936$
$n = 13$	$b = 22.3411$ grams/min
	$r^2 = 0.9985$
Aqueous Phase Output Rate	$a = -4.785531$
$n = 21$	$b = 26.3342$ grams/min
	$r^2 = 0.9983$
Insoluble Oil Output Rate	$a = -105.51$
$n = 9$	$b = 5.831$ grams/min
	$r^2 = 0.9604$

---

*Hewlett-Packard HP-19C-29C Applications Book, p. 102-106.

TABLE A-2. SEPARATION PROCESS 1-A--RAW OIL--2 STAGE EXTRACTION--CUMULATIVE REACTANT AND PRODUCT WEIGHTS

	Input		Output	
Time Min.	Raw Oil* g	Water g	Aqueous Phase g	Oil g
0	0	0	0	0
5	61	120	115	-
10	126	250	292	-
20	237	470	594	-
30	361	570	813	89
50	534	1000	1209	-
60	607	1190	1439	200
65	667	1360	1605	226
70	760	1570	1861	-
80	906	1830	2158	-
90	1001	2000	2449	369
100	1092	2250	2679	-
110	1165	2460	2960	-
120	1231	2630	3127	512
130	1328	2880	3336	-
140	1446	3150	3732	-
150	1643	3420	3982	738
160	1741	3620	4170	-
170	1789	3820	4482	-
180	1935	4000	4785	927
185	1998	4120	4805	1121

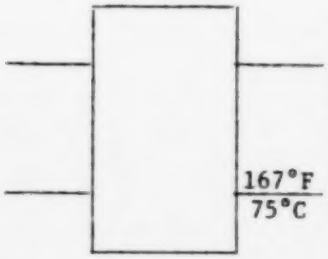
*Raw Oil Density = 1.215 g/ml

Process 1-B--Vacuum Stripped Oil--Two Stage Extraction--Total Reactant and Product Balance

Vacuum Evaporator-(Stripper)--

Raw Oil - 1932g
Water - 226.3g
Organics - 1705.7g

Steam

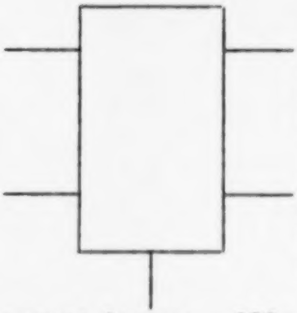


Volatiles - 284g
Water - 226.3g
Organics - 57.7g

Vacuum Stripped Oil - 1648g
Nonvolatile Organics-1621g
Volatile Organics - 27g

The raw pyrolytic oil had a water content of 11.712% and an organics content of 88.288%. The purpose of the stripping operation was to remove the water from the pyrolytic oil. However, small scale tests to strip the oil showed that the raw pyrolytic oil had a volatiles content of 14.7% (composed of 79.57% water and 20.43% organics). Thus, some organics had been volatilized in the process of stripping the water from the pyrolytic oil.

Extractor-1st Stage--



Vacuum Stripped Oil-1648g
Nonvolatile Organics-1621g
Volatile Organics -27g

Water - 2830g

Aqueous Phase - 3194g
Nonvolatile Organics - 667g
Volatile Organics - 19.3g
Water - 2507.7g

Insoluble Oil Phase-1129g
Nonvolatile Organics-903g
Volatile Organics - 6.8g
Water - 219.2g

Apparent Losses - 155g
Nonvolatile Organics - 51g
Volatile Organics - 0.9g
Water - 103.1g

TABLE A-3. FLOWRATES--RUN NO. 1B

HP-29C--Linear Curve Fit*
The data is fitted to a straight line (linear regression). The form of the equation is

$$y = a + bx$$

where x = time (min); y = accumulated stream input or output (grams)

Vacuum Stripped Oil Rate $n = 7$	$a = -19.259$ $b = 13.098$ grams/min $r^2 = 0.9741$
Water Input Rate $n = 10$	$a = -34.406$ $b = 23.297$ grams/min $r^2 = 0.9711$
Aqueous Phase Output Rate $n = 10$	$a = -58.849$ $b = 25.617$ grams/min $r^2 = 0.9925$
Insoluble Oil Output Rate $n = 4$	$a = -34.49$ $b = 8.777$ grams/min $r^2 = 0.9837$

---

*Hewlett-Packard HP-19C/HP-29C Applications Book, p. 102-106.

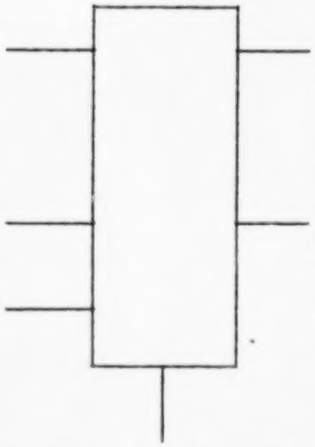
TABLE A-4. SEPARATION PROCESS 1-B--VACUUM STRIPPED OIL--2 STAGE EXTRACTION--CUMULATIVE REACTANT AND PRODUCT WEIGHTS

	Input		Output	
Time Min.	Vacuum Stripped Oil* g	Water g	Aqueous Phase g	Oil g
0	0	0	0	0
10	42	200	190	-
20	105	490	502	-
50	336	1000	1054	-
60	672	1150	1476	402
70	787	1400	1606	-
75	1113	2000	1949	657
90	1217	2280	2310	-
115	1501	2750	3013	-
130	1648	2830	3194	1129

*Vacuum stripped oil density = 1.238 g/ml

Process 2-A--Raw Oil--Simultaneous MIBK and Water Extraction--Total Reactant and Product Balance

Extractor--



Raw Oil - 555.3g
Nonvolatile Organics-472g
Volatile Organics - 38.9g
Water - 44.4g

MIBK - 562g

Water - 780g

Aqueous Phase - 1153g
Nonvolatile Organics-358g
Volatile Organics - 23.6g
Water - 748.3g
MIBK - 23.1 g

MIBK Phase - 741g
Nonvolatile Organics-114g
Volatile Organics-15.2g
Water - 74.2g
MIBK - 537.6g

Apparent Losses - 3.3g
Nonvolatile Organics - 0g
Volatile Organics - 0.1g
Water - 1.9g
MIBK - 1.3g

TABLE A-5. FLOWRATES--RUN No. 2-A

HP-29C--Linear Curve Fit*
The data is fitted to a straight line (linear regression). The form of the equation is

$$y = a + bx$$

where x = time (min); y = accumulated stream input or output (grams)

Raw Oil Input Rate	$a = 19.5851$
n = 7	$b = 6.19224$
	$r^2 = 0.98756$
Water Input Rate	$a = -31.19097$
n = 7	$b = 9.38692$
	$r^2 = 0.98394$
MIBK Input Rate	$a = -28.9572$
n = 7	$b = 6.17643$
	$r^2 = 0.98622$
Total Output Rate	$a = -74.80375$
n = 7	$b = 21.80581$
	$r^2 = 0.99509$

*Hewlett-Packard HP-19C/HP-29C Applications Book, p. 102-106.

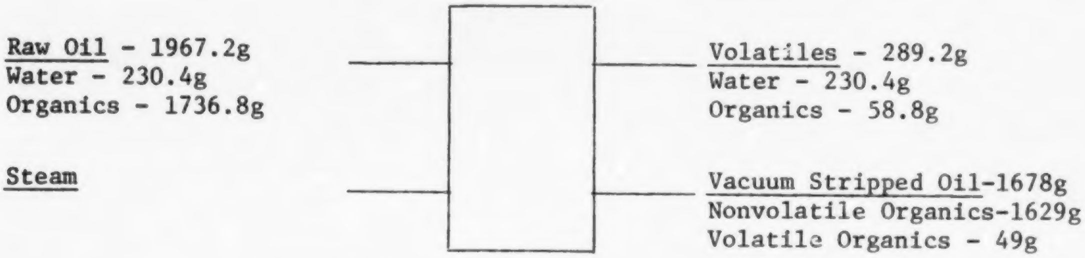
TABLE A-6. SEPARATION PROCESS 2-A--RAW OIL--SIMULTANEOUS EXTRACTION WITH MIBK AND WATER--CUMULATIVE REACTANT AND PRODUCT WEIGHTS

	Input			Output
Time Min.	Raw Oil* g	Water g	MIBK g	Total g
0	0	0	0	0
10	49.4	70	24.1	140
22	129.6	150	96.5	380
30	197.4	190	160.8	534
53	377.6	500	265.3	1009
75	499.7	720	418.0	1601
90	555.3	780	562.0	1918

*Raw Oil Density = 1.234 g/ml

Process 2-B--Vacuum Stripped Oil--Simultaneous MIBK and Water Extraction--Total Reactant and Product Balance

Vacuum Evaporator-(Stripper)--



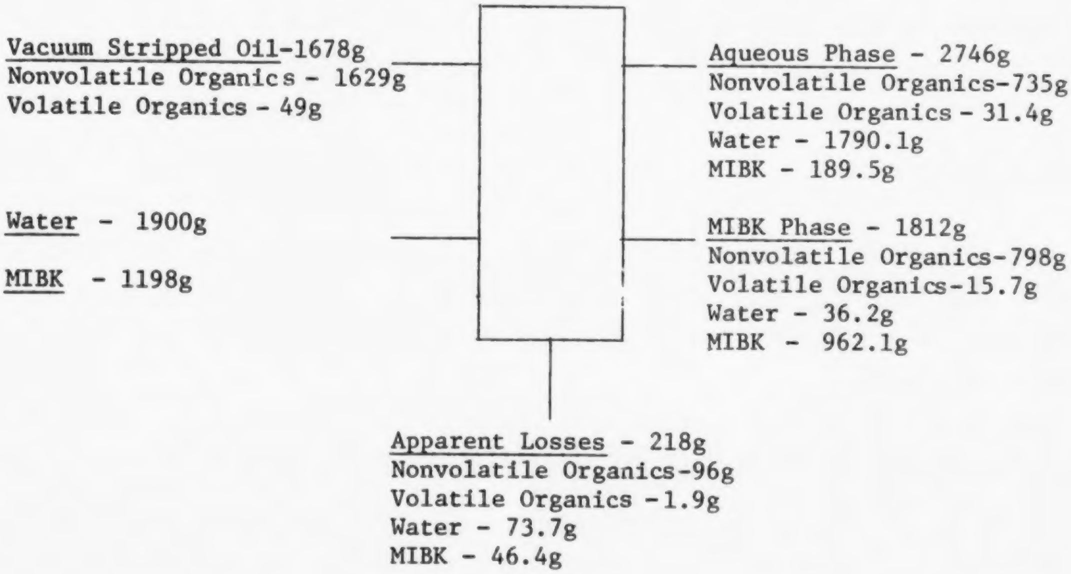
Raw Oil - 1967.2g
Water - 230.4g
Organics - 1736.8g

Steam

Volatiles - 289.2g
Water - 230.4g
Organics - 58.8g

Vacuum Stripped Oil-1678g
Nonvolatile Organics-1629g
Volatile Organics - 49g

Extractor--



Vacuum Stripped Oil-1678g
Nonvolatile Organics - 1629g
Volatile Organics - 49g

Water - 1900g

MIBK - 1198g

Aqueous Phase - 2746g
Nonvolatile Organics-735g
Volatile Organics - 31.4g
Water - 1790.1g
MIBK - 189.5g

MIBK Phase - 1812g
Nonvolatile Organics-798g
Volatile Organics-15.7g
Water - 36.2g
MIBK - 962.1g

Apparent Losses - 218g
Nonvolatile Organics-96g
Volatile Organics -1.9g
Water - 73.7g
MIBK - 46.4g

All inputs were measured quantities, as were the quantities in the Aqueous Phase and the MIBK Phase. The total amount of Apparent Losses was found by difference. Nonvolatile Organic content of the Aqueous Phase and the MIBK Phase was measured. Nonvolatile Organic content in Apparent Losses was determined by difference.

The remaining constituents of Apparent Losses (solvents and volatile organics) were calculated as explained below. Losses occurred by two methods, spillage and evaporation. It was assumed that the losses due to spillage were much greater than the losses due to evaporation. Thus, the losses of solvents and volatile organics of "apparent losses" will occur in the same proportion as their proportion in the well-mixed extractor fluid.

The percentage of volatile organics in each of the output streams was estimated to be the same as the percent volatile organics in the solvents and volatile organics portion of the input stream.

The four remaining components were the amounts of water and MIBK in both the aqueous and the MIBK phases. As stated previously the extractor effluent was a well mixed dispersion. The effluent was allowed to stand overnight to separate into 2 phases. But even after overnight settling, some MIBK remained dissolved and/or mixed in the Aqueous Phase and some water remained dissolved and/or unseparated in the MIBK phase. For design purposes it was estimated that the water content of the MIBK phase was 2%. The remainder of the mass balance was calculated. The resulting MIBK content of the aqueous phase was 6.9%.

TABLE A-7. FLOWRATES--RUN NO. 2-B

HP-29C Linear Curve Fit*
The data is fitted to a straight line (linear regression). The form of the equation is

$$y = a + bx$$

where x = time (min); y = accumulated stream input or output, (grams).

Vacuum Stripped Oil Rate	$a = -45.7056$
	$b = 13.2809$
n = 8	$r^2 = 0.99105$
Water Input Rate	$a = 1.55937$
	$b = 15.540$
n = 12	$r^2 = 0.9944$
MIBK Input Rate	$a = 48.94185$
	$b = 9.74807$
n = 11	$r^2 = 0.97695$
Total Output Rate	$a = -197.6378$
	$b = 38.4628$
n = 9	$r^2 = 0.961935$

---

*Hewlett-Packard HP-19C/HP-29C Applications Book, p. 102-106.

TABLE A-8. SEPARATION PROCESS 2-B--VACUUM STRIPPED OIL--SIMULTANEOUS EXTRACTION WITH MIBK AND WATER--CUMULATIVE REACTANT AND PRODUCT WEIGHTS

	Input			Output
Time Min.	Vacuum Stripped Oil* g	Water g	MIBK g	Total g
0	0	0	0	0
10	30	160	24	213
30	70	480	281	774
45	347	670	458	1113
60	595	920	723	1858
70	864	1000	804	2159
80	983	1320	892	2551
90	1092	1460	973	3650
100	1231	1620	1045	4116
115	1469	1800	1138	4255
120	1614	1820	1164	4306
125	1678	1900	1198	4558

* Vacuum Stripped Oil Density = 1.238g/ml

APPENDIX B

PILOT PLANT CALCULATIONS

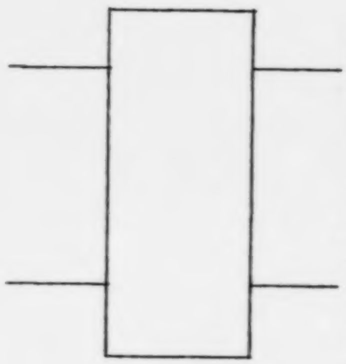
MAJOR EQUIPMENT--MATERIAL BALANCES

Process 1-A--Raw Oil--Two Stage Extraction

Extractor--1st Stage

Raw Oil - 2432.6 lb/hr
Nonvolatile Organics - 2067.3 lb/hr
Volatile Organics 170.5 lb/hr
Water - 194.8 lb/hr

Water - 5016.2 lb/hr



Aqueous Phase-6083.9 lb/hr
Nonvolatile Organics - 1071.4 lb/hr
Volatile Organics - 139.7 lb/hr
Water - 4872.8 lb/hr

Insoluble Oil Phase - 1364.8 lb/hr
Nonvolatile Organics - 995.9 lb/hr
Volatile Organics-30.8 lb/hr
Water - 338.1 lb/hr

$$\text{Raw Oil} = 4\ \text{gal/min} \left|\frac{\text{ft}^3}{7.48\ \text{gal}}\right| \frac{62.4\ \text{lb}}{\text{ft}^3} \left| 1.215 \right| \frac{60\ \text{min}}{\text{hr}} = 2432.6\ \text{lb/hr}$$

Nonvolatile Organics = 2432.6 lb/hr |1698/1998| = 2067.3 lb/hr

Volatile Organics = 2432.6 lb/hr |140/1998| = 170.5 lb/hr

Water = 2432.6 lb/hr |160/1998| = 194.8 lb/hr

Water = 2432.6 lb/hr |4120/1998| = 5016.2 lb/hr = 602 gal/hr

Aqueous Phase = 2432.6 lb/hr |(4806 + 191)/1998| = 6083.9 lb/hr

Nonvolatile Organics = 6083.9 lb/hr |(808 + 72)/4997| = 1071.4 lb/hr

Volatile Organics = 6083.9 lb/hr |(108.7 + 6.0)/4997| = 139.7 lb/hr

Water = 6083.9 lb/hr |(3889.3 + 113)/4997| = 4872.8 lb/hr

Insoluble Oil Phase = 2432.6 lb/hr |1121/1998| = 1364.8 lb/hr

Nonvolatile Organics - 1364.8 lb/hr |818/1121| = 995.9 lb/hr

Volatile Organics - 1364.8 lb/hr |25.3/1121| = 30.8 lb/hr

Water - 1364.8 lb/hr |277.7/1121| = 338.1 lb/hr

Extractor-2nd Stage

Aqueous Phase - 6083.9 lb/hr
Nonvolatile Organics - 1071.4 lb/hr
Volatile Organics - 139.7 lb/hr
Water - 4872.8 lb/hr

MIBK - 2436.6 lb/hr

MIBK Soluble Phase - 2673.7 lb/hr
MIBK - 2436.6 lb/hr
Organics - 237.1 lb/hr

Water Soluble Phase - 5846.8 lb/hr
Water - 4872.8 lb/hr
Organics - 973.97 lb/hr

$$\underline{\text{MIBK}} = 6083.9\ \text{lb/hr}\left|\frac{1200\ \text{ml MIBK}}{2400\ \text{g AQ PHASE}}\middle|\frac{0.801\text{g}}{\text{ml}}\right| = 2436.6\ \text{lb/hr}$$

From laboratory analysis 19.58% of the organics in the Aqueous Phase input stream were present in the MIBK soluble phase, and 80.42% of the organics in the Aqueous Phase input stream were present in the Water Soluble Phase.

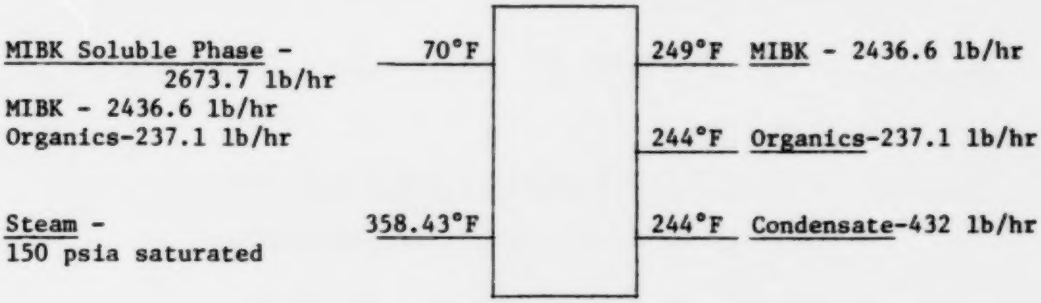
MIBK Soluble Phase

Organics = 1211.1 lb/hr |.1958| = 237.13 lb/hr

Water Soluble Phase

Organics - 1211.1 lb/hr |.8042| = 973.97 lb/hr

Evaporator--


MIBK Soluble Phase - 2673.7 lb/hr
MIBK - 2436.6 lb/hr
Organics-237.1 lb/hr
70°F
Steam - 150 psia saturated
358.43°F
249°F
MIBK - 2436.6 lb/hr
244°F
Organics-237.1 lb/hr
244°F
Condensate-432 lb/hr

$$\underline{\text{MIBK}} = 2436.6 \text{ lb/hr} \left|\frac{0.459 \text{ BTU}}{\text{LB} \cdot {}^\circ\text{F}}\right| (244 - 70)^\circ\text{F}\Big| +$$

$$2436.6 \text{ lb/hr } |82.5 \text{ BTU/lb}| + 2436.6 \text{ lb/hr} \left|\frac{0.459 \text{ BTU}}{\text{lb} \cdot {}^\circ\text{F}}\right| \cdot$$

$$|(249 - 244^\circ\text{F})| = 401{,}213 \text{ BTU/hr}$$

$\underline{\text{Organics}}$ - (Estimate cp to be 0.55 $\frac{\text{BTU}}{\text{lb} \cdot {}^\circ\text{F}}$) =

$$237.1 \text{ lb/hr} \left|\frac{0.55 \text{ BTU}}{\text{lb} \cdot {}^\circ\text{F}}\right| (244 - 70)^\circ\text{F}\Big| = 22{,}690 \text{ BTU/hr}$$

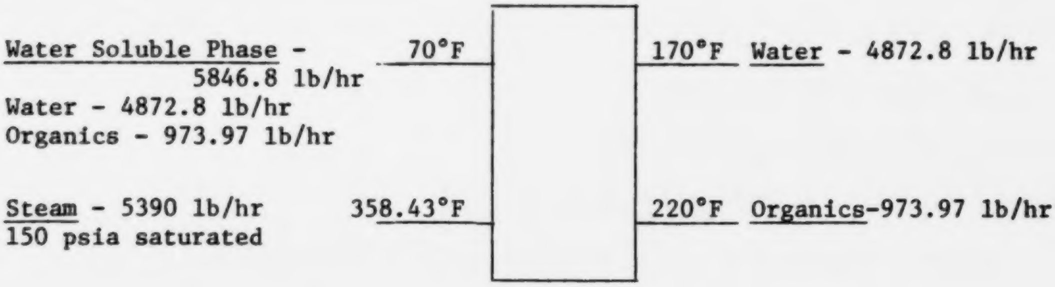
Total = 423,903 BTU/hr

$$\underline{\text{Steam Use}} = x \text{ lb/hr } |(1194.1 \text{ BTU/lb} - 1162.0 \text{ BTU/lb})| +$$

$$x \text{ lb/hr } |949.5 \text{ BTU/lb}| = 423{,}903 \text{ BTU/hr}$$

$$x = 432 \text{ lb/hr, 150 psia sat steam}$$

Vacuum Evaporator--


Water Soluble Phase - 5846.8 lb/hr
Water - 4872.8 lb/hr
Organics - 973.97 lb/hr
70°F
Steam - 5390 lb/hr
150 psia saturated
358.43°F
170°F
Water - 4872.8 lb/hr
220°F
Organics-973.97 lb/hr

Water = 4872.8 lb/hr $|(1134.2 \text{ BTU/lb} - 137.97 \text{ BTU/lb}|$

$$+\ 4872.8 \text{ lb/hr } \left|\frac{1.0 \text{ BTU}}{\text{lb} \cdot {}^\circ\text{F}}\right| (170 - 70^\circ\text{F}| = 5{,}341{,}710 \text{ BTU/hr}$$

Organics = 973.97 lb/hr $\left|\frac{0.55 \text{ BTU}}{\text{lb} \cdot {}^\circ\text{F}}\right| |(220 - 70)^\circ\text{F}| = 80{,}353$ BTU/hr

Total = 5,422,062 BTU/hr

Steam Use = x lb/hr $|(1194.1 \text{ BTU/lb} - 1153.4 \text{ BTU/lb})|$

$$+\ x \text{ lb/hr } |965.2 \text{ BTU/lb}| = 5{,}422{,}062 \text{ BTU/hr}$$

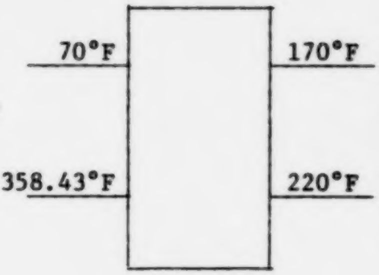
x = 5390 lb/hr steam, 150 psia saturated

Process 1-B--Vacuum Stripped Oil--Two Stage Extraction

Vacuum Evaporator-(Stripper)--

Raw Oil - 2432.6 lb/hr
Water - 284.9 lb/hr
Organics - 2147.7 lb/hr

Steam - 499 lb/hr



Volatiles - 357.6 lb/hr
Water - 284.9 lb/hr
Organics - 72.7 lb/hr

Vacuum Stripped Oil - 2075.0 lb/hr
Nonvolatile Organics - 2041.0 lb/hr
Volatile Organics-34.0 lb/hr

Raw Oil = 4 gal/min $\left|\frac{\text{ft}^3}{7.48 \text{ gal}}\right| \frac{62.4 \text{ lb}}{\text{ft}^3} | 1.215 | \frac{60 \text{ min}}{\text{hr}}| = 2432.6$ lb/hr

Water = 2432.6 lb/hr |.1171| = 284.9 lb/hr

Organics = 2432.6 lb/hr |.8829| = 2147.7 lb/hr

Volatiles = 2432.6 lb/hr |.147| = 357.6 lb/hr

Organics = 357.6 lb/hr |.2032| = 72.7 lb/hr

Water = 357.6 lb/hr |.7968| = 284.9 lb/hr

Vacuum Stripped Oil = 2432.6 lb/hr |.853| = 2075.0 lb/hr

Nonvolatile Organic = 2075.0 lb/hr |.9836| = 2041.0 lb/hr

Volatile Organic = 2075.0 lb/hr |.0164| = 34.0 lb/hr

Volatiles

$$\text{Water} = 284.9\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{f}}\right|(170 - 70)^\circ\text{F}| + 284.9\ \text{lb/hr}\ |996.2\ \text{BTU/lb}|$$

$$= 312{,}307\ \text{BTU/hr}$$

$$\text{Organics} = 72.7\ \text{lb/hr}\ \left|\frac{0.5167\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(170 - 70)^\circ\text{F}| + 72.7\ \text{lb/hr}\ |195.5\ \text{BTU/lb}|$$

$$= 17{,}969\ \text{BTU/hr}$$

$$\underline{\text{Vacuum Stripped Oil}} = 2075.0\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(220 - 70)^\circ\text{F}|$$

$$= 171{,}188\ \text{BTU/hr}$$

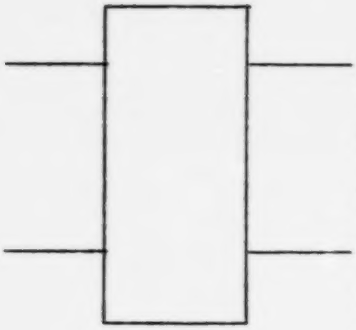
Total = 501,464 BTU/hr

$$\underline{\text{Steam Use}} = x\ \text{lb/hr}\ |(1194.1\ \text{BTU/lb} - 1153.4\ \text{BTU/lb})| + x\ \text{lb/hr}$$

$$\cdot|965.2\ \text{BTU/lb}| = 501{,}464\ \text{BTU/hr}$$

$$x = 499\ \text{lb/hr steam, 150 psia saturated}$$

Extractor-1st Stage--



Vacuum Stripped Oil - 2075.0 lb/hr
Nonvolatile Organics - 2041.0 lb/hr
Volatile Organics - 34.0 lb/hr

Water - 3563.3 lb/hr

Aqueous Phase - 4216.7 lb/hr
Nonvolatile Organics - 904.0 lb/hr
Volatile Organics - 25.4 lb/hr
Water - 3287.3 lb/hr

Insoluble Oil Phase - 1421.6 lb/hr
Nonvolatile Organics - 1137.0 lb/hr
Volatile Organics-8.6 lb/hr
Water - 276.0 lb/hr

$$\underline{\text{Water}} = 2075.0\ \text{lb/hr}\ |2830/1648| = 3563.3\ \text{lb/hr}$$

$$\underline{\text{Aqueous Phase}} = 2075.0\ \text{lb/hr}\ |(3194 + 155)/1648| = 4216.7\ \text{lb/hr}$$

$$\text{Nonvolatile Organics} = 4216.7\ \text{lb/hr}\ |(667 + 51)/3349| = 904.0\ \text{lb/hr}$$

$$\text{Volatile Organics} = 4216.7\ \text{lb/hr}\ |(19.3 + 0.9)/3349| = 25.4\ \text{lb/hr}$$

$$\text{Water} = 4216.7\ \text{lb/hr}\ |(2507.7 + 103.1)/3349| = 3287.3\ \text{lb/hr}$$

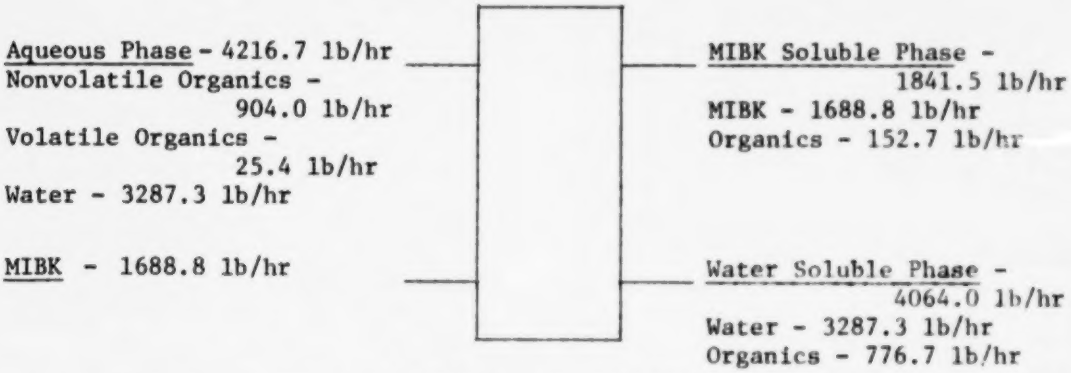
Insoluble Oil Phase = 2075.0 lb/hr |1129/1648| = 1421.6 lb/hr

Nonvolatile Organics = 1421.6 lb/hr |903/1129| = 1137.0 lb/hr

Volatile Organics = 1421.6 lb/hr |6.8/1129| = 8.6 lb/hr

Water = 1421.6 lb/hr |219.2/1129| = 276.0 lb/hr

Extractor-2nd Stage



Aqueous Phase - 4216.7 lb/hr
Nonvolatile Organics - 904.0 lb/hr
Volatile Organics - 25.4 lb/hr
Water - 3287.3 lb/hr

MIBK - 1688.8 lb/hr

MIBK Soluble Phase - 1841.5 lb/hr
MIBK - 1688.8 lb/hr
Organics - 152.7 lb/hr

Water Soluble Phase - 4064.0 lb/hr
Water - 3287.3 lb/hr
Organics - 776.7 lb/hr

$$\underline{\text{MIBK}} = 4216.7 \text{ lb/hr} \left| \frac{1200 \text{ ml MIBK}}{2400\text{g Aq Phase}} \right| \frac{0.801\text{g}}{\text{ml}} \right| = 1688.8 \text{ lb/hr}$$

From laboratory analysis 16.43% of the organics in the Aqueous Phase input stream were present in the MIBK soluble phase, and 83.57% of the organics in the aqueous phase input stream were present in the water soluble phase.

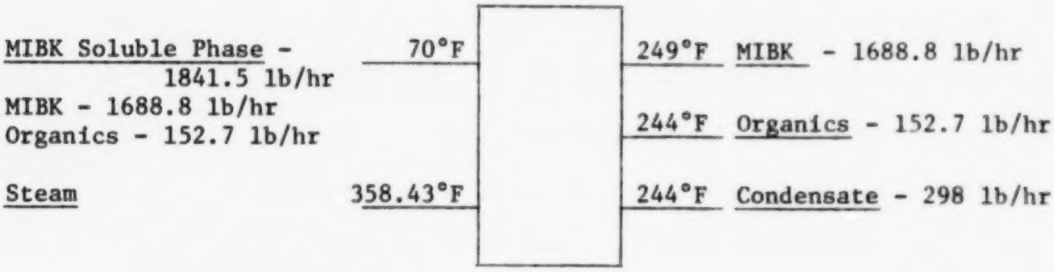
MIBK Soluble Phase

Organics = 929.4 lb/hr .1643 = 152.7 lb/hr

Water Soluble Phase

Organics = 929.4 lb/hr .8357 = 776.7 lb/hr

Evaporator--



MIBK Soluble Phase - 1841.5 lb/hr
MIBK - 1688.8 lb/hr
Organics - 152.7 lb/hr

Steam

MIBK - 1688.8 lb/hr

Organics - 152.7 lb/hr

Condensate - 298 lb/hr

$$\underline{\text{MIBK}} = 1688.8\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right| \left|(244-70)^\circ\text{F}\right| +$$

$$1688.8\ \text{lb/hr}\ \left|82.5\ \text{BTU/lb}\right| + 1688.8\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|$$

$$\cdot\left|(249-244)^\circ\text{F}\right| = 278{,}080\ \text{BTU/hr}$$

$$\underline{\text{Organics}} - (\text{Estimate cp to be } \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|) = 152.7\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|$$

$$\cdot\left|(244-70)^\circ\text{F}\right| = 14{,}613\ \text{BTU/hr}$$

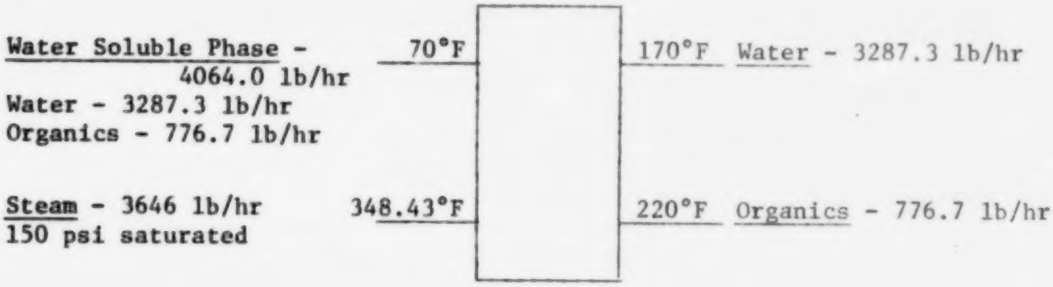
Total = 292,693 BTU/hr

$$\underline{\text{Steam Use}} = x\ \text{lb/hr}\ \left|(1194.1\ \text{BTU/lb} - 1162.0\ \text{BTU/lb})\right|$$

$$+\ x\ \text{lb/hr}\ \left|949.5\ \text{BTU/lb}\right| = 292{,}693\ \text{BTU/hr}$$

x = 298 lb/hr Steam, 150 psia sat

Vacuum Evaporator


Water Soluble Phase -
4064.0 lb/hr
Water - 3287.3 lb/hr
Organics - 776.7 lb/hr
70°F
Steam - 3646 lb/hr
150 psi saturated
348.43°F
170°F
Water - 3287.3 lb/hr
220°F
Organics - 776.7 lb/hr

$$\underline{\text{Water}} = 3287.3\ \text{lb/hr}\ \left|(1134.2\ \text{BTU/lb} - 137.97\ \text{BTU/lb})\right|$$

$$+\ 3287.3\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right| \left|(170-70)^\circ\text{F}\right| = 3{,}603{,}637\ \text{BTU/hr}$$

$$\underline{\text{Organics}} = 776.7\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right| \left|(220-70)^\circ\text{F}\right| = 64{,}078\ \text{BTU/hr}$$

Total = 3,667,715 BTU/hr

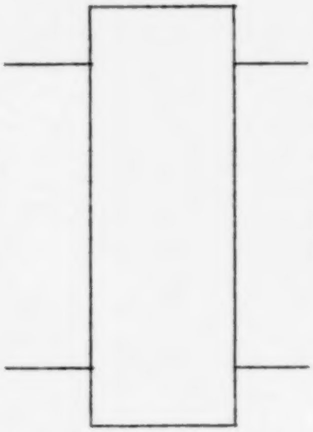
$$\underline{\text{Steam Use}} = x\ \text{lb/hr}\ \left|(1194.1\ \text{BTU/lb} - 1153.4\ \text{BTU/lb})\right| +$$

$$x\ \text{lb/hr}\ \left|965.2\ \text{BTU/lb}\right| = 3{,}667{,}715\ \text{BTU/hr}$$

x = 3,646 lb/hr steam, 150 psia saturated

Process 2-A--Raw Oil--Simultaneous MIBK and Water Extraction

Extractor



Raw Oil - 2470.6 lb/hr
Nonvolatile Organics - 2100.0 lb/hr
Volatile Organics - 173.1 lb/hr
Water - 197.5 lb/hr

MIBK - 2500.4 lb/hr

Water - 3470.3 lb/hr

Overhead Effluent - 8441.3 lb/hr
Nonvolatile Organics - 2100.0 lb/hr
Volatile Organics - 173.1 lb/hr
Water - 3667.8 lb/hr
MIBK - 2500.4 lb/hr

Insoluble Oil Phase - 0 lb/hr

$$\underline{\text{Raw Oil}} = 4\ \text{gal/min} \left|\frac{\text{ft}^3}{7.48\ \text{gal}}\right| \frac{62.4\ \text{lb}}{\text{ft}^3} \left| 1.234 \right| 60\ \text{min/hr}\right| = 2470.6\ \text{lb/hr}$$

Nonvolatile Organics = 2470.6 lb/hr |472/555.3| = 2100.0 lb/hr

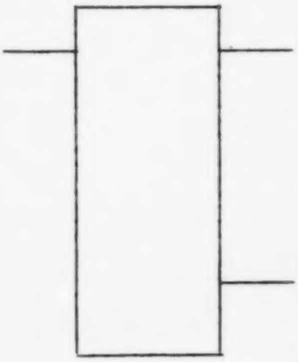
Volatile Organics = 2470.6 lb/hr |38.9/555.3| = 173.1 lb/hr

Water = 2470.6 lb/hr |44.4/555.3| = 197.5 lb/hr

MIBK = 2470.6 lb/hr |562/555.3| = 2500.4 lb/hr

Water = 2470.6 lb/hr |780/555.3| = 3470.3 lb/hr

Separator



Overhead Effluent - 8441.3 lb/hr
Nonvolatile Organics - 2100.0 lb/hr
Volatile Organics - 173.1 lb/hr
Water - 3667.8 lb/hr
MIBK - 2500.4 lb/hr

Aqueous Phase - 5144.5 lb/hr
Nonvolatile Organics - 1592.8 lb/hr
Volatile Organics - 105.4 lb/hr
Water - 3337.7 lb/hr
MIBK - 108.6 lb/hr

MIBK Phase - 3296.8 lb/hr
Nonvolatile Organics - 507.2 lb/hr
Volatile Organics-67.7 lb/hr
Water - 330.1 lb/hr
MIBK - 2391.8 lb/hr

Aqueous Phase = 8441.3 lb/hr |(1153 + 3.3)/1897.3| = 5144.5 lb/hr

Nonvolatile Organics = 5144.5 lb/hr |358/(1153 + 3.3)| = 1592.8 lb/hr

Volatile Organics = 5144.5 lb/hr |(23.6 + 0.1)/(1153 + 3.3)| = 105.4 lb/hr

Water = 5144.5 lb/hr |(748.3 + 1.9)/(1153 + 3.3)| = 3337.7 lb/hr

MIBK = 5144.5 lb/hr |(23.1 + 1.3)/(1153 + 3.3)| = 108.6 lb/hr

MIBK Phase = 8441.3 lb/hr |741/1897.3| = 3296.8 lb/hr

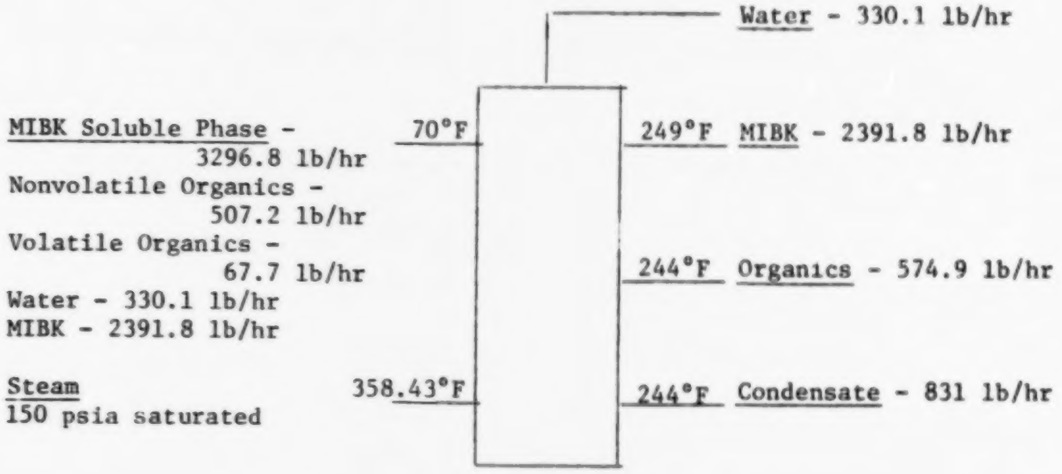
Nonvolatile Organics = 3296.8 lb/hr |114/741| = 507.2 lb/hr

Volatile Organics = 3296.8 lb/hr |15.2/741| = 67.7 lb/hr

Water = 3296.8 lb/hr |74.2/741| = 330.1 lb/hr

MIBK = 3296.8 lb/hr |537.6/741| = 2391.8 lb/hr

Evaporator (or Column)--


Water - 330.1 lb/hr
MIBK Soluble Phase - 3296.8 lb/hr
Nonvolatile Organics - 507.2 lb/hr
Volatile Organics - 67.7 lb/hr
Water - 330.1 lb/hr
MIBK - 2391.8 lb/hr
70°F
249°F
MIBK - 2391.8 lb/hr
244°F
Organics - 574.9 lb/hr
Steam
150 psia saturated
358.43°F
244°F
Condensate - 831 lb/hr

$$\underline{\text{MIBK}} = 2391.8\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ |(244 - 70)^\circ\text{F}| + 2391.8\ \text{lb/hr}$$

$$\cdot\ |82.5\ \text{BTU/lb}| + 2391.8\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ |(249 - 244)^\circ\text{F}|$$

$$= 393{,}836\ \text{BTU/hr}$$

$$\underline{\text{Organics}} - \left(\text{Estimate cp to be } 0.55 \left|\frac{\text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\right) = 574.9\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|$$

$$\cdot\ |(244 - 70)^\circ\text{F}| = 55{,}018\ \text{BTU/hr}$$

Water = $330.1\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(212-70)^\circ\text{F}\big| + \big|330.1\ \text{lb/hr}\big|970.3\ \text{BTU/lb}\big|$

= 367,170 BTU/hr

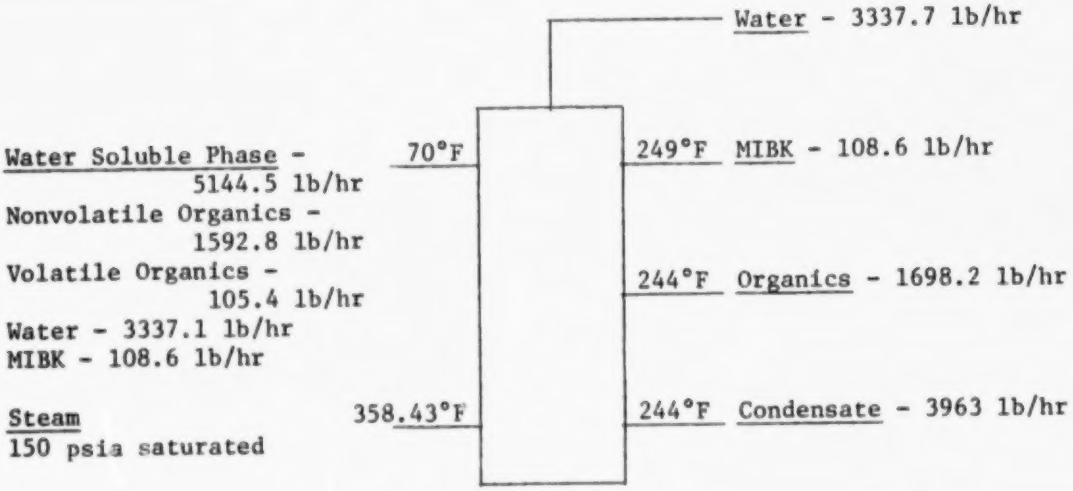
Total = 816,024 BTU/hr

Steam Use = $x\ \text{lb/hr}\ \big|(1194.1\ \text{BTU/lb} - 1162.0\ \text{BTU/lb})\big| + x\ \text{lb/hr}$

$\cdot\big|949.5\ \text{BTU/lb}\big| = 816{,}024\ \text{BTU/hr}$

x = 831 lb/hr steam, 150 psia saturated

Vacuum Evaporator (Double Effect)--



Water - 3337.7 lb/hr
Water Soluble Phase - 5144.5 lb/hr
Nonvolatile Organics - 1592.8 lb/hr
Volatile Organics - 105.4 lb/hr
Water - 3337.1 lb/hr
MIBK - 108.6 lb/hr
70°F
Steam
150 psia saturated
358.43°F
249°F
MIBK - 108.6 lb/hr
244°F
Organics - 1698.2 lb/hr
244°F
Condensate - 3963 lb/hr

Water = $3337.7\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(212-70)^\circ\text{F}\big| +$

$3337.7\ \text{lb/hr}\ \big|970.3\ \text{BTU/lb}\big| = 3{,}712{,}523\ \text{BTU/hr}$

MIBK - $108.6\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ (244-70)^\circ\text{F}\big| + 108.6\ \text{lb/hr}\left|\frac{82.5\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|$

$+\ 108.6\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(249-244)^\circ\text{F}\big| = 17{,}882\ \text{BTU/hr}$

Organics - (estimate cp to be 0.55 $\frac{\text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}$) =

$1698.2\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(244-70)^\circ\text{F}\big| = 162{,}518\ \text{BTU/hr}$

Total = 3,892,923 BTU/hr

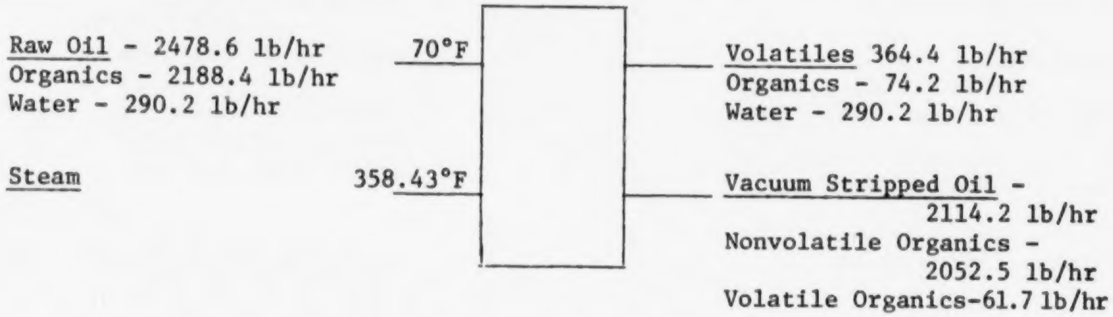
Steam Use = $x\ \text{lb/hr}\ \big|(1194.1\ \text{BTU/lb} - 1162.0\ \text{BTU/lb})\big|$

$+\ x\ \text{lb/hr}\ \big|949.5\ \text{BTU/lb}\big| = 3{,}892{,}923\ \text{BTU/hr}$

x = 3966 lb/hr steam, 150 psia saturated

Process 2-B--Vacuum Stripped Oil--Simultaneous MIBK and Water Extraction

Vacuum Evaporator-(Stripper)--


Raw Oil - 2478.6 lb/hr
Organics - 2188.4 lb/hr
Water - 290.2 lb/hr
70°F
Steam
358.43°F
Volatiles 364.4 lb/hr
Organics - 74.2 lb/hr
Water - 290.2 lb/hr
Vacuum Stripped Oil - 2114.2 lb/hr
Nonvolatile Organics - 2052.5 lb/hr
Volatile Organics-61.7 lb/hr

$$\underline{\text{Raw Oil}} = 4\ \text{gal/min}\ \left|\frac{\text{ft}^3}{7.48\ \text{gal}}\right|\frac{62.4\ \text{lb}}{\text{ft}^3}\left|1.238\ \right|60\ \text{min/hr}\right| = 2478.6\ \text{lb/hr}$$

Water = 2478.6 lb/hr |.1171| = 290.2 lb/hr

Organics = 2478.6 lb/hr |.8829| = 2188.4 lb/hr

Volatiles = 2478.6 lb/hr |.147| = 364.4 lb/hr

Organics = 364.4 lb/hr |.2032| = 74.2 lb/hr

Water = 364.4 lb/hr |.7968| = 290.3 lb/hr

Vacuum Stripped Oil = 2478.6 lb/hr |.853| = 2114.2 lb/hr

Nonvolatile Organics = 2114.2 lb/hr |1629/1678| = 2052.5 lb/hr

Volatile Organics = 2114.2 lb/hr |49/1678| = 61.7 lb/hr

Volatiles

$$\text{Water} = 290.2\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(170-70)^\circ\text{F}\right| + 290.2\ \text{lb/hr}\ |996.2\ \text{BTU/lb}|$$

= 318,217 BTU/hr

$$\text{Organics} = 74.2\ \text{lb/hr}\ \left|\frac{0.5167\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(170-70)^\circ\text{F}\right| + 74.2\ \text{lb/hr}\ |195.5\ \text{BTU/lb}|$$

= 18,340 BTU/hr

$$\text{Vacuum Stripped Oil} = 2114.2\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(220-70)^\circ\text{F}\right| = 174,422\ \text{BTU/hr}$$

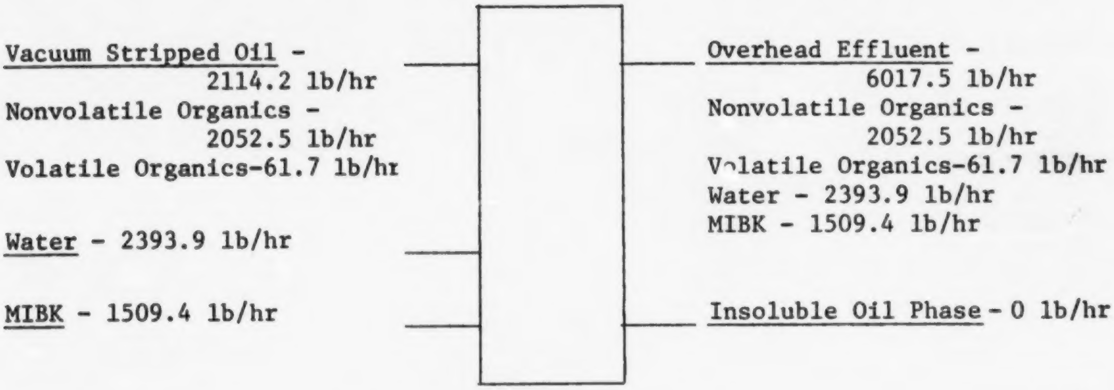
Total = 510,979 BTU/hr

Steam Use = x lb/hr |(1194.1 BTU/lb - 1153.4 BTU/lb)|

+ x lb/hr|965.2 BTU/lb| = 510,979 BTU/hr

x = 508 lb/hr steam, 150 psia saturated

Extractor--



Vacuum Stripped Oil - 2114.2 lb/hr
Nonvolatile Organics - 2052.5 lb/hr
Volatile Organics-61.7 lb/hr

Water - 2393.9 lb/hr

MIBK - 1509.4 lb/hr

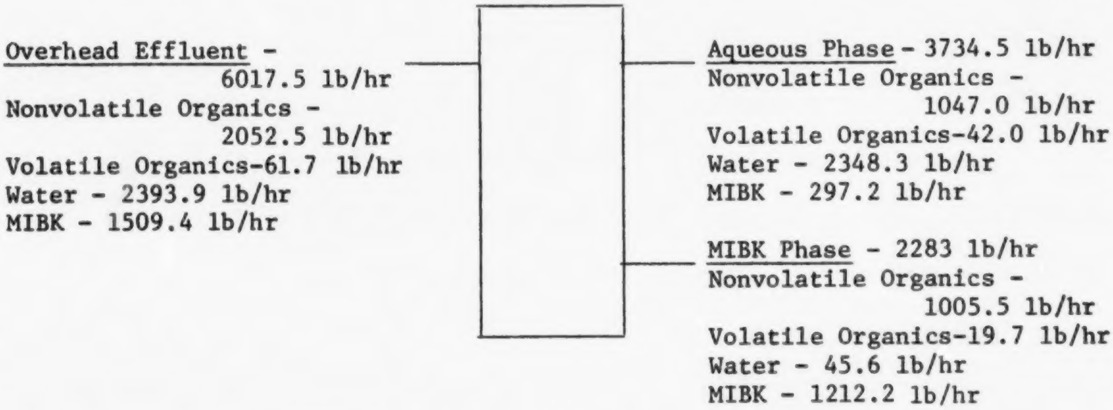
Overhead Effluent - 6017.5 lb/hr
Nonvolatile Organics - 2052.5 lb/hr
Volatile Organics-61.7 lb/hr
Water - 2393.9 lb/hr
MIBK - 1509.4 lb/hr

Insoluble Oil Phase - 0 lb/hr

$\underline{\text{MIBK}} = 2114.2 \text{ lb/hr } |1198/1678| = 1509.4 \text{ lb/hr}$

$\underline{\text{Water}} = 2114.2 \text{ lb/hr } |1900/1678| = 2393.9 \text{ lb/hr}$

Separator--



Overhead Effluent - 6017.5 lb/hr
Nonvolatile Organics - 2052.5 lb/hr
Volatile Organics-61.7 lb/hr
Water - 2393.9 lb/hr
MIBK - 1509.4 lb/hr

Aqueous Phase - 3734.5 lb/hr
Nonvolatile Organics - 1047.0 lb/hr
Volatile Organics-42.0 lb/hr
Water - 2348.3 lb/hr
MIBK - 297.2 lb/hr

MIBK Phase - 2283 lb/hr
Nonvolatile Organics - 1005.5 lb/hr
Volatile Organics-19.7 lb/hr
Water - 45.6 lb/hr
MIBK - 1212.2 lb/hr

$\underline{\text{Aqueous Phase}} = 6017.5 \text{ lb/hr } |(2746 + 218)/4776| = 3734.5 \text{ lb/hr}$

$\text{Nonvolatile Organics} = 3734.5 \text{ lb/hr } |(735 + 96)/2964| = 1047.0 \text{ lb/hr}$

$\text{Volatile Organics} = 3734.5 \text{ lb/hr } |(31.4 + 1.9)/2964| = 42.0 \text{ lb/hr}$

$\text{Water} = 3734.5 \text{ lb/hr } |(1790.1 + 73.7)/2964| = 2348.3 \text{ lb/hr}$

$\text{MIBK} = 3734.5 \text{ lb/hr } |(189.5 + 46.4)/2964| = 297.2 \text{ lb/hr}$

MIBK Phase = 6017.5 lb/hr |1812/4776| = 2283.0 lb/hr

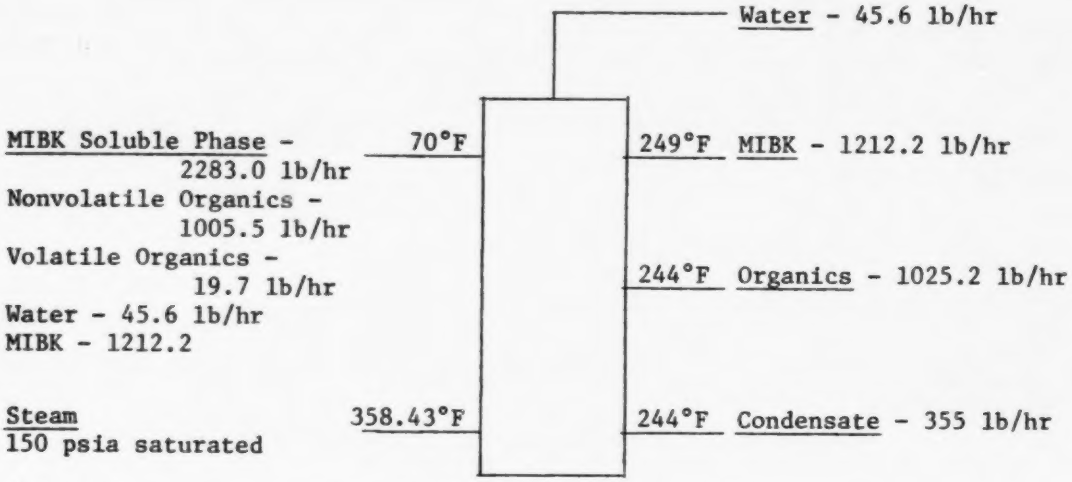
Nonvolatile Organics = 2283.0 lb/hr |798/1812| = 1005.5 lb/hr

Volatile Organic = 2283.0 lb/hr |15.7/1812| = 19.7 lb/hr

Water = 2283.0 lb/hr |36.2/1812| = 45.6 lb/hr

MIBK = 2283.0 lb/hr |962.1/1812| = 1212.2 lb/hr

Evaporator (or Column)


Water - 45.6 lb/hr
MIBK Soluble Phase - 2283.0 lb/hr
Nonvolatile Organics - 1005.5 lb/hr
Volatile Organics - 19.7 lb/hr
Water - 45.6 lb/hr
MIBK - 1212.2
70°F
249°F
MIBK - 1212.2 lb/hr
244°F
Organics - 1025.2 lb/hr
Steam
150 psia saturated
358.43°F
244°F
Condensate - 355 lb/hr

$$\text{MIBK} = 1212.2\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ \left|(244 - 70)^\circ\text{F}\right|$$

$$+\ 1212.2\ \text{lb/hr}\ |82.5\ \text{BTU/lb}| + 1212.2\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|$$

$$\cdot\left|(249 - 244)^\circ\text{F}\right| = 199{,}602\ \text{BTU/hr}$$

$$\text{Organics} - \left(\text{estimate cp to be } \frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right) = 1025.2\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|$$

$$\cdot\left|(244 - 70)^\circ\text{F}\right| = 98{,}112\ \text{BTU/hr}$$

$$\text{Water} = 45.6\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ \left|(212 - 70)^\circ\text{F}\right| + 45.6\ \text{lb/hr}\,|970.3\ \text{BTU/lb}|$$

$$= 50{,}721\ \text{BTU/hr}$$

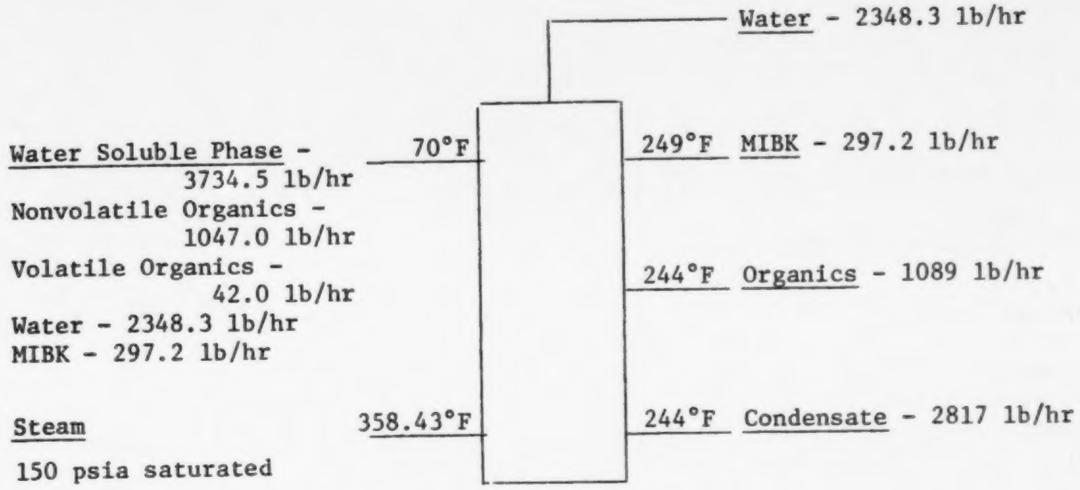
Total = 348,435 BTU/hr

$$\text{Steam Use} = x\ \text{lb/hr}\ \left|(1194.1\ \text{BTU/lb} - 1162.0\ \text{BTU/lb})\right|$$

$$+\ x\ \text{lb/hr}\ |949.5\ \text{BTU/lb}| = 348{,}435\ \text{BTU/hr}$$

x = 355 lb/hr steam, 150 psia saturated

Vacuum Evaporator (Double Effect)--


Water - 2348.3 lb/hr
Water Soluble Phase - 3734.5 lb/hr
Nonvolatile Organics - 1047.0 lb/hr
Volatile Organics - 42.0 lb/hr
Water - 2348.3 lb/hr
MIBK - 297.2 lb/hr
70°F
249°F
MIBK - 297.2 lb/hr
244°F
Organics - 1089 lb/hr
Steam
150 psia saturated
358.43°F
244°F
Condensate - 2817 lb/hr

$\underline{\text{Water}} = 2348.3\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ (212 - 70)^\circ\text{F}| +$

$2348.3\ \text{lb/hr}\ |970.3\ \text{BTU/lb}| = 2{,}612{,}014\ \text{BTU/hr}$

$\underline{\text{MIBK}} = 297.2\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ (244 - 70)^\circ\text{F}| + 297.2\ \text{lb/hr}\ |82.5\ \text{BTU/lb}$

$+\ 297.2\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ |(249 - 244)^\circ\text{F}| = 48{,}937\ \text{BTU/hr}$

$\underline{\text{Organics}}$ - (estimate cp to be $\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}$) $= 1089\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|$

$\cdot|(244 - 70)^\circ\text{F}| = 104{,}217\ \text{BTU/hr}$

$\underline{\text{Total}} = 2{,}765{,}169\ \text{BTU/hr}$

$\underline{\text{Steam Use}} = x\ \text{lb/hr}\ |(1194.1\ \text{BTU/lb} - 1162.0\ \text{BTU/lb})|$

$+\ x\ \text{lb/hr}\,|949.5\ \text{BTU/lb}| = 2{,}765{,}169\ \text{BTU/hr}$

$x = 2{,}817$ lb/hr steam, 150 psia saturated

MAJOR EQUIPMENT COST ESTIMATE

Four individual processing schemes have been investigated on the laboratory scale. Two use raw pyrolytic oil as a feed stock for extraction while two require that the raw pyrolytic oil undergo a stripping operation prior to extraction. Two processes employ two stage extraction while two processes perform a simultaneous extraction in a single stage.

The pilot plant was designed so that each of the four processes could be tested using the single pilot plant installation. For each piece of equipment, the four processes were examined to determine the largest capacity or size necessary for that particular piece of equipment. For example: process 1-B requires a 1st stage extractor with a volume of 90.96 ft^3, while process 2-A requires a volume of 149.2 ft^3. Process 2-A was used as the basis for the design calculations. The pilot plant design basis is a 4 GPM feed rate of raw pyrolytic oil into the pilot plant system. All pilot equipment is scaled up directly from experimental results.

Equipment cost estimates are taken from Peters and Timmerhouse [14], except for estimates of the extractors which are taken from an article by J. W. Drew [21]. All costs are updated to the period Nov.-Dec. 1979 using the Chemical Engineering Plant Cost Index. Installations costs are estimated to be 39% of purchased equipment costs [14]. The evaporators and strippers were not designed in detail. The heat requirements necessary to perform the particular unit operation were estimated. The results were used directly to estimate the cost of a piece of equipment that would satisfy the heat requirements. The extractor cost estimates are based on Fig. 10, which uses an arbitrary column height of 20 feet as a reference point. Although the pilot plant extractor dimensions would not be expected to be the same as those in the design calculations, the reference height of 20 feet was used to calculate the equipment cost estimate.

EQUIPMENT COSTS

Pilot Plant--Cost Summary

Raw Oil Storage Tank	(1)	$ 9,382
Raw Oil Feed Tank	(2)	9,382
Vacuum Evaporator (Stripper)	(3)	39,090
Extractor (1st Stage)	(4)	48,790
Separator (or Holdup Tank)	(5)	23,454
Extractor (2nd Stage)	(6)	48,790
MIBK Soluble - Holdup Tank	(7)	9,382
Evaporator	(8)	46,908
MIBK Holdup Tank	(9)	3,440
MIBK Soluble - Product Storage Tank	(10)	4,691
Water Soluble - Holdup Tank	(11)	9,382
Vacuum Evaporator	(12)	87,561
Water Soluble - Product Storage Tank	(13)	7,193
MIBK Storage Tank	(14)	3,440
Volatiles - Product Storage Tank	(15)	4,691
Spent Oil - Product Storage Tank	(16)	4,691
Water Storage Tank	(17)	5,629
Total Installed Equipment Cost		365,896
Instrumentation and controls - (9.35% of installed equipment cost)		34,211
Piping - (22.3% of installed equipment cost)		81,211
Electrical - (7.2% of installed equipment cost)		26,345
Total Pilot Plant Equipment Cost		$508,047

Pilot Plant Cost Estimates--Combined Scheme for all Four Continuous Extraction Processes

Raw Oil Storage Tank--(1)
Use a Tank volume of 500 gal (304ss)
From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

$$\text{Purchased cost} = \$3000 \left|\frac{246.8}{109.7}\right| = \$6749$$

$$\text{Installed cost} = \$6749|1.39| = \$9382$$

Raw Oil Feed Tank--(2)
Use a tank volume of 500 gal (304ss)
From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

$$\text{Purchased cost} = \$3000 \left|\frac{246.8}{109.7}\right| = \$6749$$

$$\text{Installed cost} = \$6749\ |1.39| = \$9,382$$

Vacuum Evaporator--(Stripper)--(3)

Heat Requirements--From Process 1-B $q = 501,464$ BTU/hr

From Process 2-B $q = 510,979$ BTU/hr

Use Process 2-B for design calculations

$$\Delta t_1 = (358.43 - 70)°F \quad \Delta t_2 = (220 - 170)°F$$

$$\Delta t_{1m} = \frac{\Delta t_1 - \Delta t_2}{\ln(\Delta t_1/\Delta t_2)} = \frac{288.43 - 50}{\ln(288.43/50)} = 136°F$$

$$q = UA\Delta t_{1m}; \quad \text{estimate } U = 200 \frac{\text{BTU}}{\text{hr}\cdot\text{ft}^2\cdot°\text{F}}$$

$$A = \frac{q}{U\Delta t_{1m}} = \frac{510,979}{200(136)} = 18.78 \text{ ft}^2$$

From Figure 14-28 [14] agitated falling-film evaporators (304ss)

$$\text{Purchased cost} = \$12,500 \left|\frac{246.8}{109.7}\right| = \$28,122$$

$$\text{Installed cost} = \$28,122\ |1.39| = \$39,090$$

Extractor-1st Stage--(4)

Process 1-A

$$\text{Raw Oil} = 2432.6 \text{ lb/hr} \left|\frac{\text{ft}^3}{62.4 \text{ lb}}\right| \left|\frac{1}{1.215}\right| \left|\frac{\text{hr}}{60 \text{ min}}\right| |65 \text{ min}| = 34.76 \text{ ft}^3$$

$$\text{Water} = 5016.2\ \text{lb/hr}\ \Big|\frac{\text{ft}^3}{62.4\ \text{lb}}\Big|\frac{\text{hr}}{60\ \text{min}}\Big|65\ \text{min}\Big| = 87.09\ \text{ft}^3$$

Total volume = 121.85 ft^3

Process 1-B

$$\text{Vacuum Stripped Oil} = 2075.0\ \text{lb/hr}\ \Big|\frac{\text{ft}^3}{62.4\ \text{lb}}\Big|\frac{1}{1.238}\Big|\frac{\text{hr}}{60\ \text{min}}\Big|65\ \text{min}\Big| = 29.10\ \text{ft}^3$$

$$\text{Water} = 3563.3\ \text{lb/hr}\ \Big|\frac{\text{ft}^3}{62.4\ \text{lb}}\Big|\frac{\text{hr}}{60\ \text{min}}\Big|65\ \text{min}\Big| = 61.86\ \text{ft}^3$$

Total Volume = 90.96 ft^3

Process 2-A

$$\text{Raw Oil} = 2470.6\ \text{lb/hr}\ \Big|\frac{\text{ft}^3}{62.4\ \text{lb}}\Big|\frac{1}{1.234}\Big|\frac{\text{hr}}{60\ \text{min}}\Big|65\ \text{min}\Big| = 34.76\ \text{ft}^3$$

$$\text{Water} = 3470.3\ \text{lb/hr}\ \Big|\frac{\text{ft}^3}{62.4\ \text{lb}}\Big|\frac{\text{hr}}{60\ \text{min}}\Big|65\ \text{min}\Big| = 60.25\ \text{ft}^3$$

$$\text{MIBK} = 2500.4\ \text{lb/hr}\ \Big|\frac{\text{ft}^3}{62.4\ \text{lb}}\Big|\frac{1}{0.801}\Big|\frac{\text{hr}}{60\ \text{min}}\Big|65\ \text{min}\Big| = 54.19\ \text{ft}^3$$

Total Volume = 149.2 ft^3

Process 2-B

$$\text{Vacuum Stripped Oil} = 2114.2\ \text{lb/hr}\ \Big|\frac{\text{ft}^3}{62.4\ \text{lb}}\Big|\frac{1}{1.238}\Big|\frac{\text{hr}}{60\ \text{min}}\Big|65\ \text{min}\Big| = 29.65\ \text{ft}^3$$

$$\text{Water} = 2393.9\ \text{lb/hr}\ \Big|\frac{\text{ft}^3}{62.4\ \text{lb}}\Big|\frac{\text{hr}}{60\ \text{min}}\Big|65\ \text{min}\Big| = 41.56\ \text{ft}^3$$

$$\text{MIBK} = 1509.4\ \text{lb/hr}\ \Big|\frac{\text{ft}^3}{62.4\ \text{lb}}\Big|\frac{1}{0.801}\Big|\frac{\text{hr}}{60\ \text{min}}\Big|65\ \text{min}\Big| = 32.72\ \text{ft}^3$$

Total Volume = 121.85 ft^3

Use Process 2-A for design calculations
Use an extractor volume of 150 ft^3 (304ss)

From Ref. [21]: $V = \frac{\pi}{4}\ d^2h$

where h is assumed to be 20 feet

$$150\ \text{ft}^3 = \frac{\pi}{4}\ d^2(20)$$

$$d = 3.09\ \text{ft or } 37.08\ \text{inches}$$

From Figure 10 [21] - Cost of Columns:

$$\text{Purchased cost} = \$32{,}000\ \Big|0.8\Big|\frac{246.8}{109.7}\Big| = \$35{,}100$$

The factor given for converting from a 316ss column to a 304ss column is 0.8.

$$\text{Installed cost} = \$35{,}100\ \Big|1.39\Big| = \$48{,}790$$

Separator (or Holdup Tank)--(5)

Use Process 2-A for design calculations

$$\text{Raw Oil} = 2470.6\ \text{lb/hr} \left| \frac{ft^3}{62.4\ lb} \right| \frac{1}{1.234} \right| = 32.085\ ft^3/hr$$

$$\text{MIBK} = 2500.4\ \text{lb/hr} \left| \frac{ft^3}{62.4\ lb} \right| \frac{1}{0.801} \right| = 50.026\ ft^3/hr$$

$$\text{Water} = 3470.3\ \text{lb/hr} \left| \frac{ft^3}{62.4\ lb} \right| = 55.61\ ft^3/hr$$

$$\text{Total Volume} = 137.72\ ft^3/hr \left| \frac{7.48\ gal}{ft^3} \right| = 1030\ gal/hr$$

Choose a 3 hour Holdup = 3090 gal
Use a separator volume of 3000 gal (304ss)
From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

$$\text{Purchased cost} = \$7500 \left| \frac{246.8}{109.7} \right| = \$16{,}873$$

$$\text{Installed cost} = \$16{,}873 \left| 1.39 \right| = \$23{,}454$$

Extractor-2nd Stage-- (6)

Process 1-A

$$\text{Aqueous Phase} = 6083.9\ \text{lb/hr} \left| \frac{ft^3}{62.4\ lb} \right| \frac{1}{1.235} \left| \frac{hr}{60\ min} \right| 65\ min \right| = 85.52\ ft^3$$

$$\text{MIBK} = 2436.6\ \text{lb/hr} \left| \frac{ft^3}{62.4\ lb} \right| \frac{1}{0.801} \left| \frac{hr}{60\ min} \right| 65\ min \right| = 52.81\ ft^3$$

Total volume = 138.34 ft^3

Process 2-A

$$\text{Aqueous Phase} = 4216.7\ \text{lb/hr} \left| \frac{ft^3}{62.4\ lb} \right| \frac{1}{1.235} \left| \frac{hr}{60\ min} \right| 65\ min \right| = 59.28\ ft^3$$

$$\text{MIBK} = 1688.8\ \text{lb/hr} \left| \frac{ft^3}{62.4\ lb} \right| \frac{1}{0.801} \left| \frac{hr}{60\ min} \right| 65\ min \right| = 36.60\ ft^3$$

Total Volume = 95.88 ft^3

Use an extractor volume of 150 ft^3 (304ss)

From Ref. [21]: $V = \frac{\pi}{4} d^2 h$

where h is assumed to be 20 feet

$$150\ ft^3 = \frac{\pi}{4} d^2 (20)$$

$$d = 307\ ft^2 \text{ or } 37.08 \text{ inches}$$

From Figure 10 [21] - Cost of columns:

Purchased cost = $\$32{,}000 \,|0.8| \left|\frac{246.8}{109.7}\right| = \$35{,}100$

The factor given for converting from a 316ss column to a 304ss column is 0.8.

Installed cost = $\$35{,}100 \,|1.39| = \$48{,}790$

MIBK Soluble--Holdup Tank--(7)
Use a tank volume of 500 gal (304ss)
From Figure 13-56 [1 4] Cost of mixing, storage, and pressure tanks:

Purchased cost = $\$3000 \left|\frac{246.8}{109.7}\right| = \$6749$

Installed cost = $\$6749 \,|1.39| = \$9382$

Evaporator (MIBK Phase)-- (8)

Heat Requirements--From Process 1-A $q = 423{,}903$ BTU/hr

From Process 1-B $q = 292{,}693$ BTU/hr

From Process 2-A $q = 816{,}024$ BTU/hr

From Process 2-B $q = 348{,}435$ BTU/hr

Use Process 2-A for design calculations

$$\Delta t_1 = (244 - 70)^\circ\text{F} \qquad \Delta t_2 = (358.43 - 249)^\circ\text{F}$$

$$\Delta t_{1m} = \frac{\Delta t_1 - \Delta t_2}{\ln(\Delta t/\Delta t_2)} = \frac{174 - 109.43}{\ln(174/109.43)} = 139.23^\circ\text{F}$$

$$q = UA\Delta t_{1m}; \quad \text{Estimate } U = 200 \frac{\text{BTU}}{\text{hr}\cdot\text{ft}^2\cdot{}^\circ\text{F}}$$

$$A = \frac{q}{U\Delta t_{1m}} = \frac{816{,}024}{200(139.23)} = 29.30 \text{ ft}^2$$

From Figures 14-28 [1 4] agitated falling-film evaporators (304ss)

Purchased cost = $\$15{,}000 \left|\frac{246.8}{109.7}\right| = \$33{,}747$

Installed cost = $\$33{,}747 \,|1.39| = \$46{,}908$

MIBK Holdup Tank--(9)

Use Process 1-A for design calculations

MIBK = $2436.6 \text{ lb/hr} \left|\frac{\text{ft}^3}{62.4 \text{ lb}}\right| \left|\frac{1}{0.801}\right| = 48.75 \text{ ft}^3\text{/hr}$

Capacity = $47.75 \text{ ft}^3\text{/hr} \,|7.48 \text{ gal/ft}^3| = 364.6$ gal/hr

Choose a 3 hour Holdup = 1094 gal
Use a tank volume of 1100 gal (C-S)
From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = $1100 $\left|\frac{246.8}{109.7}\right|$ = $2475

Installed cost = $2475 |1.39| = $3440

MIBK Soluble - Product Storage Tank-- (10)
Use Process 2-B for design calculations

MIBK Soluble Organics = 1025.2 lb/hr $\left|\frac{ft^3}{62.4\ lb}\right|\frac{1}{1.235}\right|$ = 13.3 ft^3/hr

Capacity = 13.3 ft^3/hr $|7.48\ gal/ft^3|$ = 99.5 gal/hr

Use a tank volume of 150 gal (304ss)
From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = $1500 $\left|\frac{246.8}{109.7}\right|$ = $3375

Installed cost = $3375 |1.39| = $4691

Water soluble-Holdup Tank--(11)
Use a tank volume of 500 gal (304ss)
From Figures 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = $3000 $\left|\frac{246.8}{109.7}\right|$ = $6749

Installed cost = $6749 |1.39| = $9382

Vacuum Evaporator (Water Soluble Phase)--(12)

Heat Requirements--From Process 1-A q = 5,422,062 BTU/hr

Process 1-B q = 3,667,715 BTU/hr

Process 2-A q = 3,892,923 BTU/hr

Process 2-B q = 2,765,169 BTU/hr

Use Process 1-A for design calculations

$$\Delta t_1 = (220 - 70)°F \quad \Delta t_2 = (358.43 - 220)°F$$

$$\Delta t_{1m} = \frac{\Delta t_1 - \Delta t_2}{\ln(\Delta t_1/\Delta t_2)} = \frac{150 - 138.43}{\ln(150/138.43)} = 144°F$$

$$q = UA\ t_{1m}; \quad \text{Estimate } U = 500\ BTU\ \frac{BTU}{hr \cdot ft^2 \cdot °F}$$

$$A = \frac{q}{U\Delta t_{1m}} = \frac{5,422,062}{500(144)} = 75.3\ ft^2$$

From Figure 14-28 [14] Agitated falling-film evaporators (304ss)

Purchased cost = \$28,000 $\left|\frac{246.8}{109.7}\right|$ = \$62,994

Installed cost = \$62,994 $|1.39|$ = \$87,561

Water Soluble - Product Storage Tank--(13)
Use Process 2-A for design calculations

Water Soluble Organics = 1698.2 lb/hr $\left|\frac{ft^3}{62.4 \text{ lb}}\right| \left|\frac{1}{1.235}\right|$ = 22.04 ft^3/hr

Capacity = 22.04 ft^3/hr $|7.48 \text{ gal}/ft^3|$ = 164.8 gal/hr

Use a tank volume of 300 gal (304ss)
From Figures 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = \$2300 $\left|\frac{246.8}{109.7}\right|$ = \$5174

Installed cost = \$5174 $|1.39|$ = \$7193

MIBK Storage Tank--(14)
Use a tank volume of 1100 gal (C-S)
From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = \$1100 $\left|\frac{246.8}{109.7}\right|$ = \$2475

Installed cost = \$2475 $|1.39|$ = \$3440

Volatiles-Product Storage Tank--(15)
Use Process 2-B for design calculations

Volatiles--

Organics = 74.1 lb/hr $\left|\frac{ft^3}{62.4 \text{ lb}}\right| \left|\frac{1}{1.047}\right|$ = 1.134 ft^3/hr

Water = 290.3 lb/hr $\left|\frac{ft^3}{62.4 \text{ lb}}\right|$ = 4.652 ft^3/hr

Total Volume = 5.786 ft^3/hr $\left|\frac{7.48 \text{ gal}}{ft^3}\right|$ = 43.28 gal/hr

Choose a 3 hour Holdup = 129.8 gal
Use a tank volume of 150 gal (304ss)
From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = \$1500 $\left|\frac{246.8}{109.7}\right|$ = \$3375

Installed cost = \$3375 $|1.39|$ = \$4691

Spent Oil Storage Tank-- (16)
Use Process 1-A for design calculations

Insoluble Oil Phase--

$$\text{Organics} = 1026.7\ \text{lb/hr}\ \left|\frac{\text{ft}^3}{62.4\ \text{lb}}\right|\left|\frac{1}{1.234}\right| = 13{,}334\ \text{ft}^3\text{/hr}$$

$$\text{Water} = 338.1\ \text{lb/hr}\ \left|\frac{\text{ft}^3}{62.4\ \text{lb}}\right| = 5.42\ \text{ft}^3\text{/hr}$$

$$\text{Total Volume} = 18.76\ \text{ft}^3\text{/hr}\ \left|\frac{7.48\ \text{gal}}{\text{ft}^3}\right| = 140\ \text{gal/hr}$$

Use a tank volume of 150 gal (304ss)
From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

$$\text{Purchased cost} = \$1500\ \left|\frac{246.8}{109.7}\right| = \$3375$$

$$\text{Installed cost} = \$3375\ |1.39| = \$4691$$

Water Storage Tank--(17)
Use Process 1-A for design calculations

$$\text{Water} = 5016.2\ \text{lb/hr}\ \left|\frac{\text{ft}^3}{62.4\ \text{lb}}\right| = 80.39\ \text{ft}^3\text{/hr}$$

$$\text{Capacity} = 80.39\ \text{ft}^3\text{/hr}\ |7.48\ \text{gal/ft}^3| = 601.3\ \text{gal/hr}$$

Choose a 3 hour Holdup = 1804 gal
Use a tank volume of 200 gal (C-S)
From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

$$\text{Purchased cost} = \$1800\ \left|\frac{246.8}{109.7}\right| = \$4050$$

$$\text{Installed cost} = \$4050\ |1.39| = \$5629$$

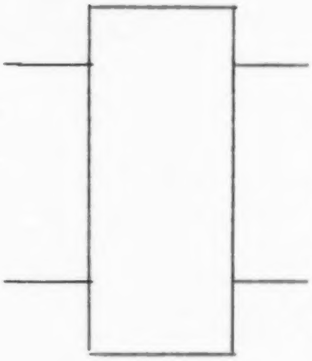
APPENDIX C

COMMERCIAL PLANT CALCULATIONS

MAJOR EQUIPMENT--MATERIAL BALANCES

Process 1-A--Raw Oil--Two Stage Extraction

Extractor-1st Stage--



Raw Oil - 9000 lb/hr
Nonvolatile Organics - 7648.7 lb/hr
Volatile Organics - 630.6 lb/hr
Water - 720.7 lb/hr

Water - 18,558.6 lb/hr

Aqueous Phase - 22,509 lb/hr
Nonvolatile Organics - 3964.0 lb/hr
Volatile Organics - 516.7 lb/hr
Water - 18,028.3 lb/hr

Insoluble Oil Phase - 5049.6 lb/hr
Nonvolatile Organics - 3684.7 lb/hr
Volatile Organics - 114.0 lb/hr
Water - 1250.9 lb/hr

Raw Oil

Nonvolatile Organics = 9000 lb/hr |1698/1998| = 7648.7 lb/hr

Volatile Organics = 9000 lb/hr |140/1998| = 630.6 lb/hr

Water = 9000 lb/hr |160/1998| = 720.7 lb/hr

Water = 9000 lb/hr |4120/1998| = 18,558.6 lb/hr

Aqueous Phase = 9000 lb/hr |(4806 + 191)/1998| = 22,509 lb/hr

Nonvolatile Organics = 22,509 lb/hr |(808 + 72)/4997| = 3964.0 lb/hr

Volatile Organics = 22,509 lb/hr |(108.7 + 6.0/4997| = 516.7 lb/hr

Water = 22,509 lb/hr |(3889.3 + 113)/4997| = 18,028.3 lb/hr

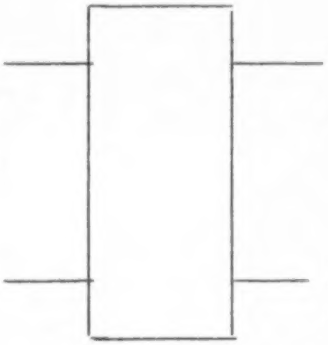
Insoluble Oil Phase = 9000 lb/hr |1121/1998| = 5049.6 lb/hr

Nonvolatile Organics = 5049.6 lb/hr |818/1121| = 3684.7 lb/hr

Volatile Organics = 5049.6 lb/hr |25.3/1121| = 114.0 lb/hr

Water = 5049.6 lb/hr |277.7/1121| = 1250.9 lb/hr

Extractor--2nd Stage



Aqueous Phase-22,509 lb/hr
Nonvolatile Organics - 3,964.0 lb/hr
Volatile Organics - 516.7 lb/hr
Water - 18,028.3 lb/hr

MIBK - 9014.9 lb/hr

MIBK Soluble Phase - 9,892.2 lb/hr
MIBK - 9,014.9 lb/hr
Organics - 877.3 lb/hr

Water Soluble Phase - 21,631.7 lb/hr
Water - 18,028.3 lb/hr
Organics - 3603.4 lb/hr

$$\text{MIBK} = 22{,}509 \text{ lb/hr} \left|\frac{1200 \text{ ml MIBK}}{2400\text{g Aq Phase}}\right|\left|\frac{.801\text{g}}{\text{ml}}\right| = 9014.9 \text{ lb/hr}$$

From laboratory analysis 19.58% of the organics in the Aqueous Phase input stream were present in the MIBK Soluble Phase, and 80.42% of the Organics in the Aqueous Phase input stream were present in the Water Soluble Phase.

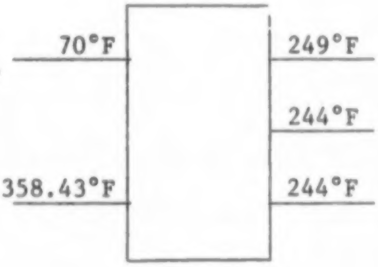
MIBK Soluble Phase

Organics = 4480.7 lb/hr |.1958| = 877.3 lb/hr

Water Soluble Phase

Organics = 4480.7 lb/hr |.8042| = 3603.4 lb/hr

Evaporator--



MIBK Soluble Phase - 9892.2 lb/hr
MIBK - 9014.9 lb/hr
Organics - 877.3 lb/hr

Steam
150 psia saturated

MIBK - 9014.9 lb/hr

Organics - 877.3 lb/hr

Condensate - 1598 lb/hr

$$\underline{\text{MIBK}} = 9014.9\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ (244.70)^\circ\text{F}\ \Big| + 9014.9\ \text{lb/hr}\ \big|82.5\ \text{BTU/lb}\big|$$

$$+\ 9014.9\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ (249-244)^\circ\text{F}\Big| = 1{,}484{,}402\ \text{BTU/hr}$$

$$\underline{\text{Organics}} - \left(\text{estimate cp to be } \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\right) = 877.3\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|$$

$$\cdot\big|(244-70)^\circ\text{F}\big| = 83.958\ \text{BTU/hr}$$

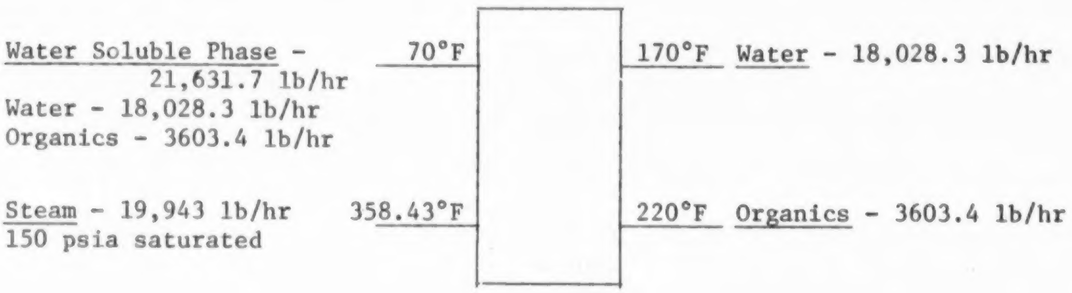
$$\underline{\text{Total}} = 1{,}568{,}360\ \text{BTU/hr}$$

$$\underline{\text{Steam Use}} = x\ \text{lb/hr}\big|(1194.1\ \text{BTU/lb} - 1162.0\ \text{BTU/lb})\big| + x\ \text{lb/hr}$$

$$\cdot\big|949.5\ \text{BTU/lb}\big| = 1{,}568{,}360\ \text{BTU/hr}$$

$$x = 1{,}598\ \text{lb/hr steam}\quad 150\ \text{psia saturated}$$

Vacuum Evaporator--



Water Soluble Phase - 21,631.7 lb/hr
Water - 18,028.3 lb/hr
Organics - 3603.4 lb/hr
70°F
Steam - 19,943 lb/hr
150 psia saturated
358.43°F
170°F
Water - 18,028.3 lb/hr
220°F
Organics - 3603.4 lb/hr

$$\underline{\text{Water}} = 18{,}028.3\ \text{lb/hr}\ \big|(1134.2\ \text{BTU/lb} - 137.97\ \text{BTU/lb})\big|$$

$$+\ 18{,}028.3\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ (170-70)^\circ\text{F}\Big| = 19{,}763{,}163\ \text{BTU/hr}$$

$$\underline{\text{Organics}} = 3603.4\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ (220-70)^\circ\text{F}\Big| = 297{,}281\ \text{BTU/hr}$$

$$\underline{\text{Total}} = 20{,}060{,}444\ \text{BTU/hr}$$

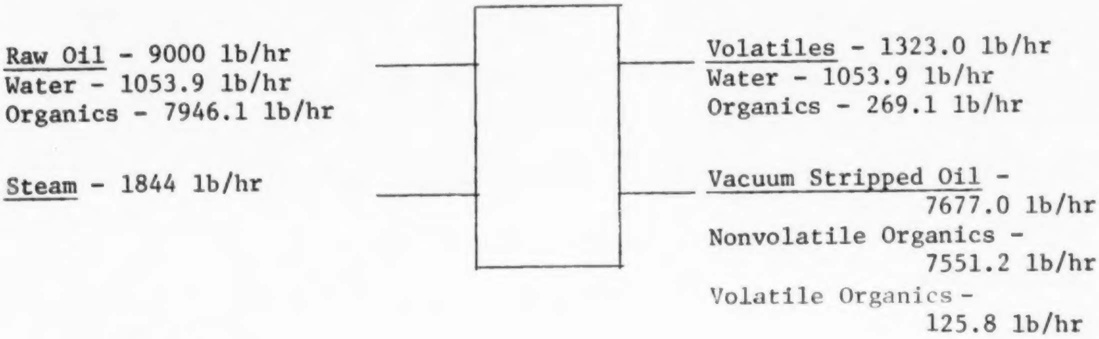
$$\underline{\text{Steam Use}} = x\ \text{lb/hr}\big|(1194.1\ \text{BTU/lb} - 1153.4\ \text{BTU/lb})\big| + x\ \text{lb/hr}$$

$$\cdot\big|965.2\ \text{BTU/lb}\big| = 20{,}060{,}444\ \text{BTU/hr}$$

$$x = 19{,}943\ \text{lb/hr steam}\quad 150\ \text{psia saturated}$$

Process 1-B--Vacuum Stripped Oil--Two Stage Extraction

Vacuum Evaporator (Stripper)--


Raw Oil - 9000 lb/hr
Water - 1053.9 lb/hr
Organics - 7946.1 lb/hr
Steam - 1844 lb/hr
Volatiles - 1323.0 lb/hr
Water - 1053.9 lb/hr
Organics - 269.1 lb/hr
Vacuum Stripped Oil - 7677.0 lb/hr
Nonvolatile Organics - 7551.2 lb/hr
Volatile Organics - 125.8 lb/hr

Raw Oil

Organics = 9000 lb/hr |.8829| = 7946.1 lb/hr

Water = 9000 lb/hr |.1171| = 1053.9 lb/hr

Volatiles = 9000 lb/hr |.147| = 1323.0 lb/hr

Organics = 1323.0 lb/hr |.2034| = 269.1 lb/hr

Water = 1323.0 lb/hr |.7966| = 1053.9 lb/hr

Vacuum Stripped Oil = 9000 lb/hr |.853| = 7677.0 lb/hr

Nonvolatile Organics = 7677 lb/hr |1621/1648| = 7551.2 lb/hr

Volatile Organics = 7677 lb/hr |27/1648| = 125.8 lb/hr

Volatiles

$$\text{Water} = 1053.9\ \text{lb/hr} \left|\frac{1.0\ \text{BTU}}{\text{lb} \cdot {}^\circ\text{F}}\right|(170 - 70)^\circ\text{F}| + 1053.9\ \text{lb/hr}|996.2\ \text{BTU/hr}|$$

$$= 1{,}155{,}285\ \text{BTU/hr}$$

$$\text{Organics} = 269.1\ \text{lb/hr} \left|\frac{0.5167\ \text{BTU}}{\text{lb} \cdot {}^\circ\text{F}}\right| (170 - 70)^\circ\text{F}| + 269.1\ \text{lb/hr}\ |195.5\ \text{BTU/lb}|$$

$$= 66{,}513\ \text{BTU/hr}$$

$$\text{Vacuum Stripped Oil} = 7677.0\ \text{lb/hr} \left|\frac{0.55\ \text{BTU}}{\text{lb} \cdot {}^\circ\text{F}}\right| (220 - 70)^\circ\text{F}|$$

$$= 633.353\ \text{BTU/hr}$$

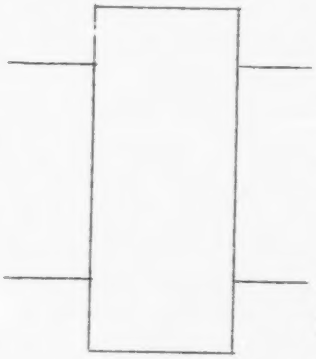
Total = 1,855,151 BTU/hr

Steam Use =x lb/hr |(1194.1 BTU/lb - 1153.4 BTU/lb)| + x lb/hr

·|965.2 BTU/lb| = 1,855,151 BTU/hr

x = 1844 lb/hr steam 150 psia saturated

Extractor-1st Stage--



Vacuum Stripped Oil 7677.0 lb/hr
Nonvolatile Organics - 7551.2 lb/hr
Volatile Organics - 125.8 lb/hr

Water - 13,183.2 lb/hr

Aqueous Phase-15,600.9 lb/hr
Nonvolatile Organics - 3344.7 lb/hr
Volatile Organics-94.1 lb/hr
Water - 12,162.1 lb/hr

Insoluble Oil Phase - 5259.3 lb/hr
Nonvolatile Organics - 4206.5 lb/hr
Volatile Organics - 31.7 lb/hr
Water - 1021.1 lb/hr

Water = 7677.0 lb/hr |2830/1648| = 13,183.2 lb/hr

Aqueous Phase = 7677.0 lb/hr |(3194 + 155)/1648| = 15,600.9 lb/hr

Nonvolatile Organics = 15,600.9 lb/hr |(667 + 51)/3349| = 3344.7 lb/hr

Volatile Organics = 15,600.9 lb/hr |(19.3 + 0.9)/3349| = 94.1 lb/hr

Water = 15,600.9 lb/hr |(2507.7 + 103.1)/3349| = 12,162.1 lb/hr

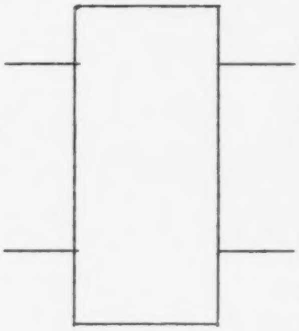
Insoluble Oil Phase = 7677.0 lb/hr |1129/1648| = 5259.3 lb/hr

Nonvolatile Organics = 5259.3 lb/hr |903/1129| = 4206.5 lb/hr

Volatile Organics = 5259.3 lb/hr |6.8/1129| = 31.7 lb/hr

Water = 5259.3 lb/hr |219.2/1129| = 1021.1 lb/hr

Extractor-2nd Stage--



Aqueous Phase-15,600.9 lb/hr
Nonvolatile Organics - 3344.7 lb/hr
Volatile Organics-94.1 lb/hr
Water - 12,162.1 lb/hr

MIBK - 6248.2 lb/hr

MIBK Soluble Phase - 6813.2 lb/hr
MIBK - 6248.2 lb/hr
Organics - 565.0 lb/hr

Water Soluble Phase - 15,035.9 lb/hr
Water - 12,162.1 lb/hr
Organics - 2873.8 lb/hr

$$\underline{\text{MIBK}} = 15{,}600.9\ \text{lb/hr}\ \left|\frac{1200\ \text{ml MIBK}}{2400\text{g Aq Phase}}\right|\frac{.801\text{g}}{\text{ml}}\right| = 6248.2\ \text{lb/hr}$$

From laboratory analysis 16.43% of the organics in the Aqueous Phase input stream were present in the MIBK Soluble Phase, and 83.57% of the organics in the Aqueous Phase input stream were present in the Water Soluble Phase.

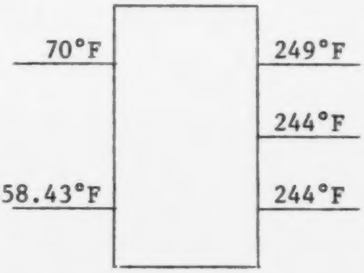
MIBK Soluble Phase

$$\text{Organics} = 3438.8\ \text{lb/hr}\ |.1643| = 565.0\ \text{lb/hr}$$

Water Soluble Phase

$$\text{Organics} = 3438.8\ \text{lb/hr}\ |.8357| = 2873.8\ \text{lb/hr}$$

Evaporator--



MIBK Soluble Phase - 6813.2 lb/hr
MIBK - 6248.2 lb/hr
Organics - 565.0 lb/hr

Steam

70°F

358.43°F

249°F MIBK - 6248.2 lb/hr

244°F Organics - 565.0 lb/hr

244°F Condensate - 1103 lb/hr

$$\text{MIBK} = 6248.2\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(244-70)^\circ\text{F}\right| + 6248.2\ \text{lb/hr}$$

$$\cdot\left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(249-244)^\circ\text{F}\right| = 1{,}028{,}836\ \text{BTU/hr}$$

$$\underline{\text{Organics}} - (\text{estimate cp to be } \frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}} = 565.0\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|$$

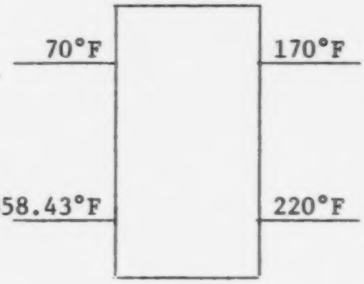
$$\cdot\left|(244-70)^\circ\text{F}\right| = 54{,}071\ \text{BTU/hr}$$

Total = 1,082,907 BTU/hr

$$\underline{\text{Steam Use}} = x \text{ lb/hr } \left|(1194.1 \text{ BTU/lb} - 1162.0 \text{ BTU/lb})\right| + x \text{ lb/hr} \cdot \left|949.5 \text{ BTU/lb}\right| = 1{,}082{,}907 \text{ BTU/hr}$$

$$x = 1103 \text{ lb/hr steam 150 psia saturated}$$

Vacuum Evaporator--



Water Soluble Phase - 15,035.9 lb/hr
Water - 12,162.1 lb/hr
Organics - 2873.8 lb/hr

Steam - 13,490 lb/hr
150 psia saturated

Water - 12,162.1 lb/hr

Organics - 2873.8 lb/hr

$$\underline{\text{Water}} = 12{,}162.1 \text{ lb/hr } \left|(1134.2 \text{ BTU/lb} - 137.97 \text{ BTU/lb})\right| + 12{,}162.1 \text{ lb/hr } \left|\frac{1.0 \text{ BTU}}{\text{lb} \cdot {}^\circ\text{F}}\right| \left|(170 - 70)^\circ\text{F}\right| = 13{,}332{,}459 \text{ BTU/lb}$$

$$\underline{\text{Organics}} = 2873.8 \text{ lb/hr } \left|\frac{0.55 \text{ BTU}}{\text{lb} \cdot {}^\circ\text{F}}\right| \left|(220 - 70)^\circ\text{F}\right| = 237{,}089 \text{ BTU/hr}$$

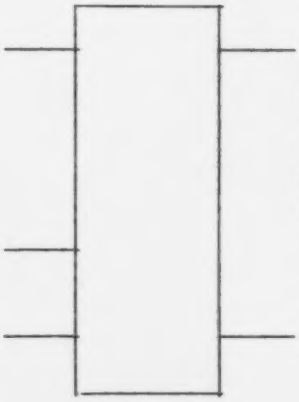
$$\underline{\text{Total}} = 13{,}569{,}548 \text{ BTU/hr}$$

$$\underline{\text{Steam Use}} = x \text{ lb/hr } \left|(1194.1 \text{ BTU/lb} - 1153.4 \text{ BTU/lb})\right| + x \text{ lb/hr } \left|965.2 \text{ BTU/lb}\right| = 13{,}569{,}548 \text{ BTU/hr}$$

$$x = 13{,}490 \text{ lb/hr steam, 150 psia saturated}$$

Process 2-A--Raw Oil--Simultaneous MIBK and Water Extraction

Extractor--



Raw Oil - 9000 lb/hr
Nonvolatile Organics - 7649.9 lb/hr
Volatile Organics - 630.5 lb/hr
Water - 719.6 lb/hr

MIBK - 9108.6 lb/hr

Water - 12,641.8 lb/hr

Overhead Effluent - 30,750.4 lb/hr
Nonvolatile Organics - 7649.9 lb/hr
Volatile Organics-630.5 lb/hr
Water - 13,361.4 lb/hr
MIBK - 9108.6 lb/hr

Insoluble Oil Phase - 0 lb/hr

Raw Oil

Nonvolatile Organics = 9000 lb/hr |472/555.3| = 7649.9 lb/hr

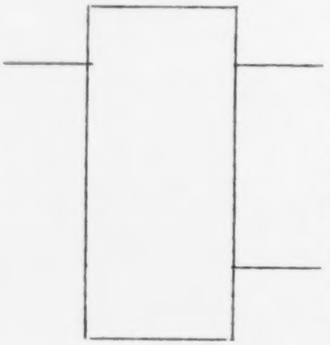
Volatile Organics = 9000 lb/hr |38.9/555.3| = 630.5 lb/hr

Water = 9000 lb/hr |44.4/555.3| = 719.6 lb/hr

Water = 9000 lb/hr |780/555.3| = 12,641.8 lb/hr

MIBK = 9000 lb/hr |562/55.3| = 9108.6 lb/hr

Separator--



Overhead Effluent - 30,750.4 lb/hr
Nonvolatile Organics - 7649.9 lb/hr
Volatile Organics - 630.5 lb/hr

Water - 13,361.4 lb/hr
MIBK - 9,108.6 lb/hr

Aqueous Phase-18,740.7 lb/hr
Nonvolatile Organics - 5802.3 lb/hr
Volatile Organics-384.1 lb/hr
Water - 12,158.8 lb/hr
MIBK - 395.5

MIBK Phase-12,009.7 lb/hr
Nonvolatile Organics - 1847.6 lb/hr
Volatile Organics - 246.4 lb/hr
Water - 1202.6 lb/hr
MIBK - 8713.1 lb/hr

Aqueous Phase = 30,750.4 lb/hr |(1153 + 3.3)/1897.3| = 18,740.7 lb/hr

Nonvolatile Organics = 18,740.7 lb/hr |358/1156.3| = 5802.3 lb/hr

Volatile Organics = 18,740.7 lb/hr |(23.6 + 0.1)/1156.3| = 384.1 lb/hr

Water = 18,740.7 lb/hr |(748.3 + 0.9)/1156.3| = 12,158.8 lb/hr

MIBK = 18,740.7 lb/hr |(23.1 + 0.3)/1156.3| = 395.5 lb/hr

MIBK Phase = 30,750.4 lb/hr |741/1897.3| = 12,009.7 lb/hr

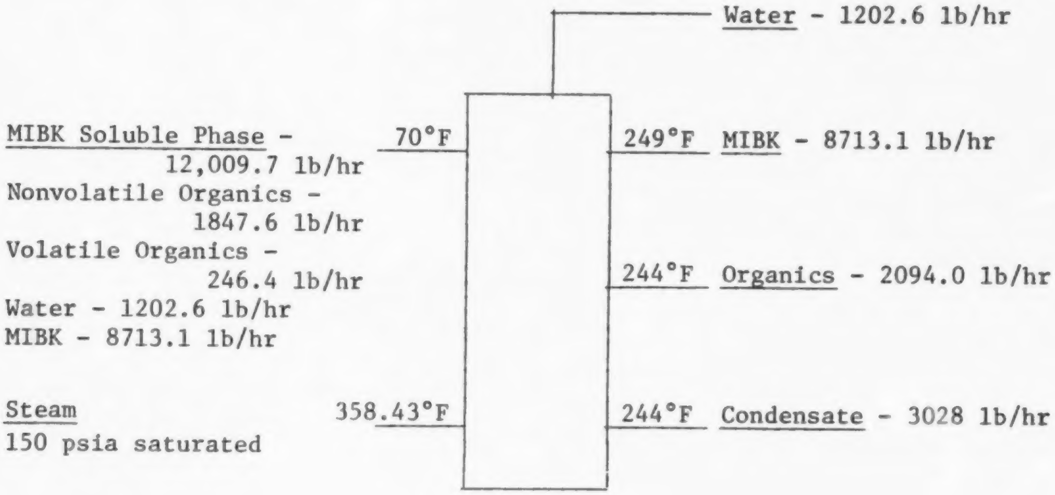
Nonvolatile Organics = 12,009.7 lb/hr |114/741| = 1847.6 lb/hr

Volatile Organics = 12,009.7 lb/hr |15.2/741| = 246.4 lb/hr

Water = 12,009.7 lb/hr |74.2/741| = 1,202.6 lb/hr

MIBK = 12,009.7 lb/hr |537.6/741| = 8,713.1 lb/hr

Evaporator (or Column)--


Water - 1202.6 lb/hr
MIBK Soluble Phase - 12,009.7 lb/hr
Nonvolatile Organics - 1847.6 lb/hr
Volatile Organics - 246.4 lb/hr
Water - 1202.6 lb/hr
MIBK - 8713.1 lb/hr
70°F
249°F
MIBK - 8713.1 lb/hr
244°F
Organics - 2094.0 lb/hr
Steam
150 psia saturated
358.43°F
244°F
Condensate - 3028 lb/hr

$$\underline{\text{MIBK}} = 8713.1\ \text{lb/hr}\left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(244-70)^\circ\text{F}\Big| + 8713.1\ \text{lb/hr}\Big|\cdot$$

$$\Big|82.5\ \text{BTU/lb}\Big| + 8713.1\ \text{lb/hr}\left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(249-244)^\circ\text{F}\Big| =$$

$$1{,}434{,}708\ \text{BTU/hr}$$

$$\underline{\text{Organics}} = \left(\text{estimate cp to be } \frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right) = 2094.0\ \text{lb/hr}\left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\cdot$$

$$\Big|(244-70)^\circ\text{F}\Big| = 200{,}396\ \text{BTU/hr}$$

$$\underline{\text{Water}} = 1202.6\ \text{lb/hr}\left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(212-70)^\circ\text{F}\Big| + 1202.6\ \text{lb/hr}\Big|\cdot$$

$$\Big|970.3\ \text{BTU/lb} = 1{,}337{,}652\ \text{BTU/hr}$$

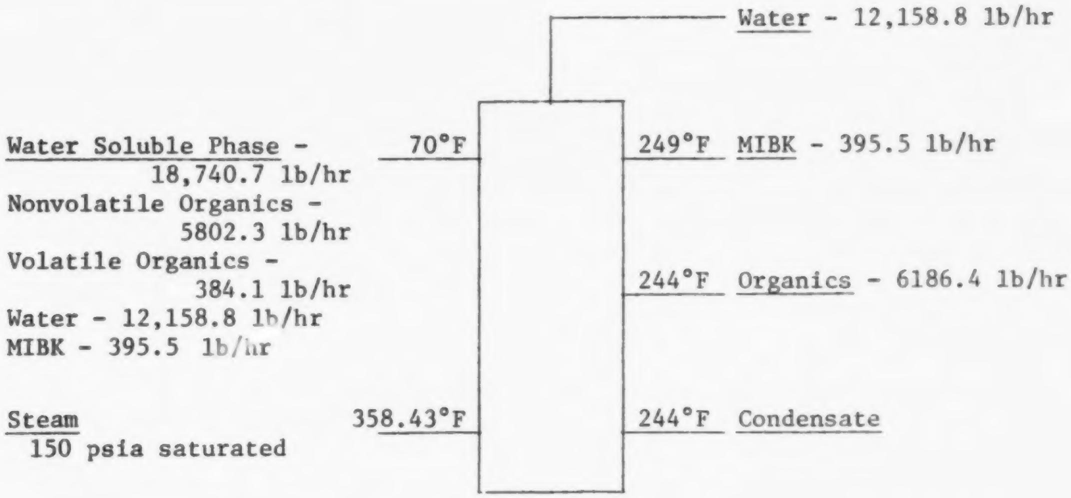
$$\underline{\text{Total}} = 2{,}972{,}756\ \text{BTU/hr}$$

$$\underline{\text{Steam Use}} = x\ \text{lb/hr}\ \Big|(1194.1\ \text{BTU/lb} - 1162.0\ \text{BTU/lb})\Big| +$$

$$x\ \text{lb/hr}\ \Big|949.5\ \text{BTU/lb}\Big| = 2{,}972{,}756\ \text{BTU/hr}$$

$$x = 3{,}028\ \text{lb/hr steam, 150 psia saturated}$$

Vacuum Evaporator (Double Effect)--


Water - 12,158.8 lb/hr
Water Soluble Phase - 18,740.7 lb/hr
Nonvolatile Organics - 5802.3 lb/hr
Volatile Organics - 384.1 lb/hr
Water - 12,158.8 lb/hr
MIBK - 395.5 lb/hr
70°F
249°F
MIBK - 395.5 lb/hr
244°F
Organics - 6186.4 lb/hr
Steam
150 psia saturated
358.43°F
244°F
Condensate

$$\underline{\text{Water}} = 12{,}158.8\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^{\circ}\text{F}}\right|\ (212 - 70)^{\circ}\text{F}\,\big| + 12{,}158.8\ \text{lb/hr}\ \big|$$

$$\cdot\,|970.3\ \text{BTU/lb}| = 13{,}524{,}233\ \text{BTU/hr}$$

$$\underline{\text{MIBK}} = 395.5\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^{\circ}\text{F}}\right|\ (244 - 70)^{\circ}\text{F}\,\big| + 395.5\ \text{lb/hr}\ \big|\cdot$$

$$|82.5\ \text{BTU/lb}|\ + 395.5\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^{\circ}\text{F}}\right|\ (249 - 244)^{\circ}\text{F}\,\big| =$$

$$65{,}124\ \text{BTU/hr}$$

$$\underline{\text{Organics}} = \left(\text{estimate cp to be } \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^{\circ}\text{F}}\right|\right) = 6186.4\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^{\circ}\text{F}}\right|$$

$$\cdot\,|(244 - 70)^{\circ}\text{F}| = 592{,}038\ \text{BTU/hr}$$

$$\underline{\text{Total}} = 14{,}181{,}395\ \text{BTU/hr}$$

$$\underline{\text{Steam Use}} = x\ \text{lb/hr}\ |(1194.1\ \text{BTU/lb} - 1162.0\ \text{BTU/lb})| +$$

$$x\ \text{lb/hr}\ |949.5\ \text{BTU/lb}| = 14{,}181{,}395\ \text{BTU/hr}$$

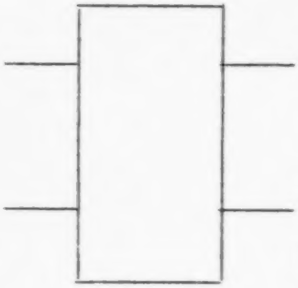
$$x = 14{,}447\ \text{lb/hr steam, 150 psia saturated}$$

Process 2-B--Vacuum Stripped Oil--Simultaneous MIBK and Water Extraction--

Vacuum Evaporator (Stripper)--

Raw Oil - 9000 lb/hr
Organics - 7946.1 lb/hr
Water - 1053.9 lb/hr

Steam - 1844 lb/hr



Volatiles - 1323.0 lb/hr
Organics - 269.1 lb/hr
Water - 1053.9 lb/hr

Vacuum Stripped Oil - 7677.0 lb/hr
Nonvolatile Organics - 7452.8 lb/hr
Volatile Organics 224.2 lb/hr

Raw Oil

Organics = 9000 lb/hr $|.8829|$ = 7946.1 lb/hr

Water = 9000 lb/hr $|.1171|$ = 1053.9 lb/hr

Volatiles = 9000 lb/hr $|.147|$ = 1323.0 lb/hr

Organics = 1323.0 lb/hr $|.2034|$ = 269.1 lb/hr

Water = 1323.0 lb/hr $|.7966|$ = 1053.9 lb/hr

Vacuum Stripped Oil = 9000 lb/hr $|.853|$ = 7677.0 lb/hr

Nonvolatile Organics = 7677.0 lb/hr $|1629/1678|$ = 7452.8 lb/hr

Volatile Organics = 7677.0 lb/hr $|49/1678|$ = 224.2 lb/hr

Volatiles

$$\text{Water} = 1053.9\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\left|(170-70)^\circ\text{F}\right| + 1053.9\ \text{lb/hr}\ \left|996.2\ \text{BTU/lb}\right|$$

$$= 1{,}155{,}285\ \text{BTU/hr}$$

$$\text{Organics} = 269.1\ \text{lb/hr}\ \left|\frac{0.5167\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\left|(170-70)^\circ\text{F}\right| + \left|269.1\ \text{lb/hr}\right|\ 195.5\ \text{BTU/lb}\right|$$

$$= 66{,}513\ \text{BTU/hr}$$

$$\text{Vacuum Stripped Oil} = 7677.0\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\left|(220-70)^\circ\text{F}\right| = 633{,}353\ \text{BTU/hr}$$

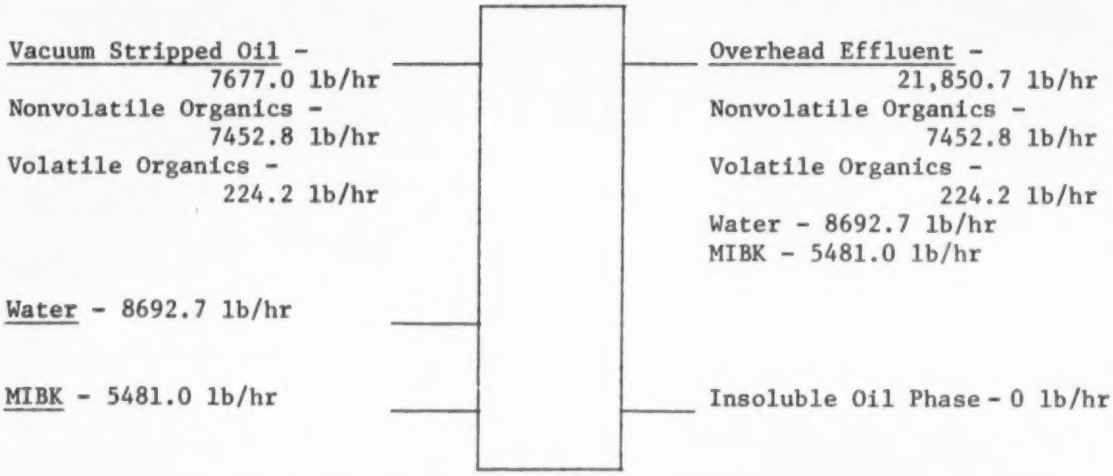
Total = 1,855,151 BTU/hr

Steam Use = x lb/hr $|(1194.1\ \text{BTU/lb} - 1153.4\ \text{BTU/lb})|$

+ x lb/hr $|965.2\ \text{BTU/lb}|$ = 1,855,151 BTU/hr

x = 1844 lb/hr steam, 150 psia saturated

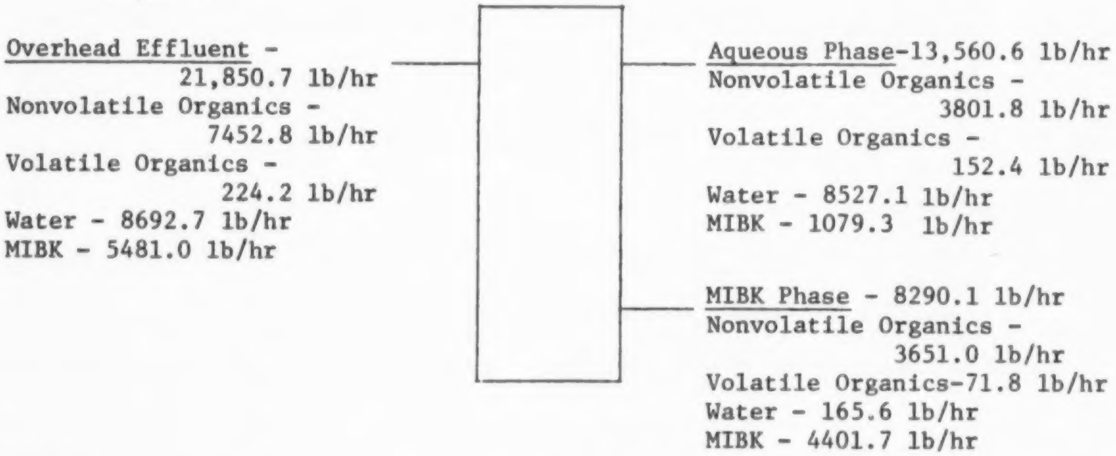
Extractor--


Vacuum Stripped Oil - 7677.0 lb/hr
Nonvolatile Organics - 7452.8 lb/hr
Volatile Organics - 224.2 lb/hr
Water - 8692.7 lb/hr
MIBK - 5481.0 lb/hr
Overhead Effluent - 21,850.7 lb/hr
Nonvolatile Organics - 7452.8 lb/hr
Volatile Organics - 224.2 lb/hr
Water - 8692.7 lb/hr
MIBK - 5481.0 lb/hr
Insoluble Oil Phase - 0 lb/hr

MIBK = 7677.0 lb/hr |1198/1678| = 5481.0 lb/hr

Water = 7677.0 lb/hr |1900/1678| = 8692.7 lb/hr

Separator--


Overhead Effluent - 21,850.7 lb/hr
Nonvolatile Organics - 7452.8 lb/hr
Volatile Organics - 224.2 lb/hr
Water - 8692.7 lb/hr
MIBK - 5481.0 lb/hr
Aqueous Phase-13,560.6 lb/hr
Nonvolatile Organics - 3801.8 lb/hr
Volatile Organics - 152.4 lb/hr
Water - 8527.1 lb/hr
MIBK - 1079.3 lb/hr
MIBK Phase - 8290.1 lb/hr
Nonvolatile Organics - 3651.0 lb/hr
Volatile Organics-71.8 lb/hr
Water - 165.6 lb/hr
MIBK - 4401.7 lb/hr

Aqueous Phase = 21,850.7 lb/hr |(2746 + 218)/4776| = 13,560.6 lb/hr

Nonvolatile Organics = 13,560.6 lb/hr |(735 + 96)/2964| = 3801.8 lb/hr

Volatile Organics = 13,560.6 lb/hr |(31.4 + 1.9)/2964| = 152.4 lb/hr

Water = 13,560.6 lb/hr |(1790.1 + 73.7)/2964| = 8527.1 lb/hr

MIBK = 13,560.6 lb/hr |(189.5 + 46.4)/2964| = 1079.3 lb/hr

MIBK Phase = 21,850.7 lb/hr |1812/4776| = 8290.1 lb/hr

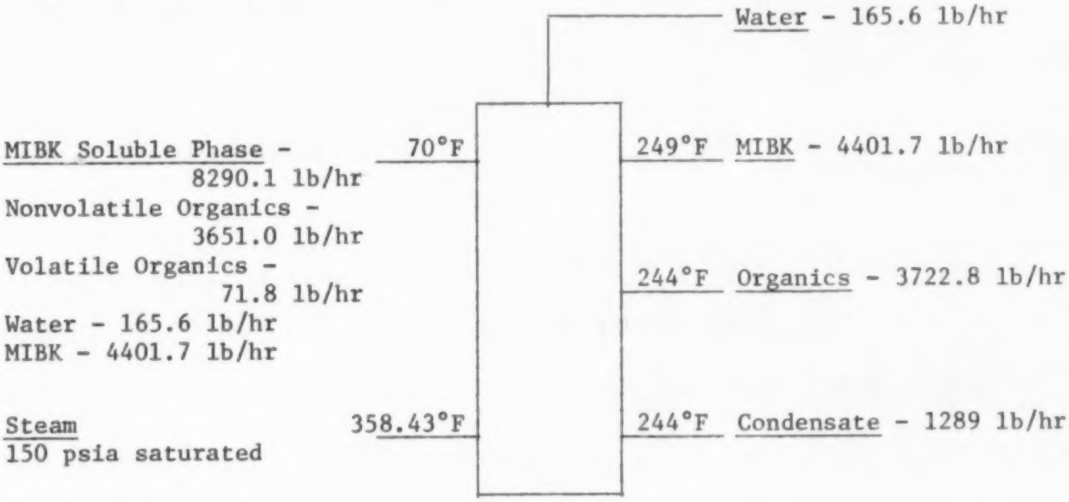
Nonvolatile Organics = 8290.1 lb/hr |798/1812| = 3651.0 lb/hr

Volatile Organics = 8290.1 lb/hr |15.7/1812| = 71.8 lb/hr

Water = 8290.1 lb/hr |36.2/1812| = 165.6 lb/hr

MIBK = 8290.1 lb/hr |962.1/1812| = 4401.7 lb/hr

Evaporator (or Column)--


Water - 165.6 lb/hr
MIBK Soluble Phase - 8290.1 lb/hr
Nonvolatile Organics - 3651.0 lb/hr
Volatile Organics - 71.8 lb/hr
Water - 165.6 lb/hr
MIBK - 4401.7 lb/hr
70°F
249°F
MIBK - 4401.7 lb/hr
244°F
Organics - 3722.8 lb/hr
Steam
150 psia saturated
358.43°F
244°F
Condensate - 1289 lb/hr

$$\underline{\text{MIBK}} = 4401.7\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(244-70)^\circ\text{F}\big| + 4401.7\ \text{lb/hr}\big|\cdot$$

$$|82.5\ \text{BTU/lb}| + 4401.7\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|(249-244)^\circ\text{F}|$$

$$= 724{,}788\ \text{BTU/hr}$$

$$\underline{\text{Organics}} = (\text{estimate cp to be } \frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}) = 3722.8\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\cdot$$

$$|(244-70)^\circ\text{F}| = 356{,}272\ \text{BTU/hr}$$

$$\underline{\text{Water}} = 165.6\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right|\ (212-70)^\circ\text{F}| + 165.6\ \text{lb/hr}|\cdot$$

$$|(970.3\ \text{BTU/lb}| = 184{,}197\ \text{BTU/hr}$$

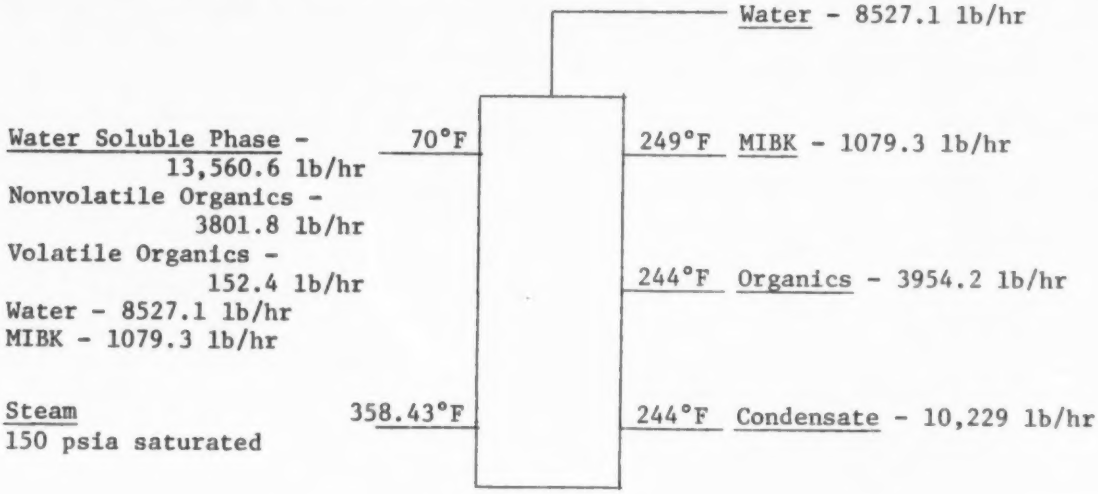
Total = 1,265,257 BTU/hr

Steam Use = x lb/hr |(1194.1 BTU/lb - 1162.0 BTU/lb)|

+ x lb/hr |949.5 BTU/lb| = 1,265,257 BTU/hr

x = 1289 lb/hr steam, 150 psia saturated

Vacuum Evaporator (Double Effect)--


Water - 8527.1 lb/hr
Water Soluble Phase - 13,560.6 lb/hr
Nonvolatile Organics - 3801.8 lb/hr
Volatile Organics - 152.4 lb/hr
Water - 8527.1 lb/hr
MIBK - 1079.3 lb/hr
70°F
249°F
MIBK - 1079.3 lb/hr
244°F
Organics - 3954.2 lb/hr
Steam
150 psia saturated
358.43°F
244°F
Condensate - 10,229 lb/hr

$$\underline{\text{Water}} = 8527.1\ \text{lb/hr}\ \left|\frac{1.0\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right| |(212 - 70)^\circ\text{F}| + 8527.1\ \text{lb/hr}| \cdot$$

$$|970.3\ \text{BTU/lb}| = 9{,}484{,}693\ \text{BTU/hr}$$

$$\underline{\text{MIBK}} = 1079.3\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right| (244 - 70)^\circ\text{F}| + 1079.3\ \text{lb/hr}| \cdot$$

$$|82.5\ \text{BTU/lb}| + 1079.3\ \text{lb/hr}\ \left|\frac{0.459\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right| |(249 - 244)^\circ\text{F}|$$

$$= 177{,}718\ \text{BTU/hr}$$

$$\underline{\text{Organics}} = (\text{estimate cp to be } \frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}) = 3954.2\ \text{lb/hr}\ \left|\frac{0.55\ \text{BTU}}{\text{lb}\cdot{}^\circ\text{F}}\right| \cdot$$

$$|(244 - 70)^\circ\text{F}| = 378{,}417\ \text{BTU/hr}$$

$$\underline{\text{Total}} = 10{,}040{,}828\ \text{BTU/hr}$$

$$\underline{\text{Steam Use}} = x\ \text{lb/hr}\ |(1194.1\ \text{BTU/lb} - 1162.0\ \text{BTU/lb})|$$

$$+\ x\ \text{lb/hr}\ |949.5\ \text{BTU/lb}| = 10{,}040{,}828\ \text{BTU/hr}$$

$$x = 10{,}229\ \text{lb/hr steam, 150 psia saturated}$$

MAJOR EQUIPMENT COST ESTIMATE

Total installed equipment cost estimates were developed for each of the four extraction processes. The equipment cost summary for each of the processes is shown below. Detailed equipment cost estimate calculations are included for Process 1-B only, as an example.

The plant design basis is a 9000 lb/hr or 14.3 GPM feed rate of raw pyrolytic oil into the plant. All equipment is scaled up directly from experimental results.

Equipment cost estimates are taken from Peters and Timmerhouse [14] except for estimates of the extractors which are taken from an article by J. W. Drew [21]. All costs are updated to the period Nov. - Dec. 1979 using the Chemical Engineering Plant Cost Index. Installation costs are estimated to be 39% of purchased equipment costs [14].

The evaporators and strippers were not designed in detail. The heat requirements necessary to perform the particular unit operation were estimated. The results were used to directly, to estimate the cost of a piece of equipment that would satisfy the heat requirements. The extractor cost estimates are based on Drew [21], which uses an arbitrary column height of 20 feet as a reference point. Although the plant extractor dimensions would not be expected to be the same as those in the design calculations, the reference height of 20 feet was used to calculate the equipment cost estimate.

EQUIPMENT COSTS

Process 1B--(2 Stage Continuous Extraction--Vacuum Stripped Oil)--Cost Summary

Raw Oil Storage Tank	1	$187,631
Raw Oil Feed Tank	2	9,382
Vacuum Evaporator - Raw Oil	3	78,180
Volatiles Storage Tank	4	73,489
Extractor - 1st Stage	5	77,758
Water Storage Tank	6	46,908
MIBK Storage Tank	7	139,472
Spent Oil Storage Tank	8	7,505
Holdup Tank	9	35,963
Extractor - 2nd Stage	10	80,808
MIBK Soluble - Holdup Tank	11	28,145
Evaporator	12	51,599
MIBK Holdup Tank	13	28,145
MIBK Soluble - Product Storage	14	39,090
Water Soluble - Holdup Tank	15	36,901
Vacuum Evaporator	16	150,105
Water Soluble - Product Storage Tank	17	101,008
Total Installed Equipment Cost		$1,172,089

Raw Oil Storage Tank-- 1

Raw Oil = 9000 lb/hr $\left|\frac{ft^3}{62.4\ lb}\right|\left|\frac{1}{1.215}\right|$ = 118.7 ft^3/hr

Capacity = 118.7 ft^3/hr |7.48 gal/ft^3| = 887.9 gal/hr

Assume a two week supply = 887.9 gal/hr |24 hr/da | 14 da| = 298,348 gal

Use a tank volume of 300,000 gal (304ss)
From Figures 13-59 [14] Storage Tanks:

Purchased cost = \$16,000 |3.75 |246.8/109.7| = \$134,986

The factor for converting from C-steel to 304ss is 3.75.

Installed cost = \$134,986 |1.39| = \$187,631

Raw Oil Feed Tank-- 2

Raw Oil = 9000 lb/hr $\left|\frac{ft^3}{62.4\ lb}\right|\left|\frac{1}{1.215}\right|$ = 118.7 ft^3/hr

Capacity = 118.7 ft^3/hr |7.48 gal/ft^3| = 887.8 gal/hr

Choose a 4 hour Holdup = 474.8 gal
Use a tank volume of 500 gal (304ss)
From Figures 13-56 [14] Cost of Mixing, storage, and pressure tanks:

Purchased cost = \$3000 |246.8/109.7| = \$6749

Installed cost = \$6749 |1.39| = \$9382

Vacuum Evaporator (Stripper)-- 3

Heat requirements -- q = 1,855,151 BTU/hr

$$\Delta t_1 = (358.43 - 70)°F \quad \Delta t_2 = (220 - 170)°F$$

$$\Delta t_{1m} = \frac{\Delta t_1 - \Delta t_2}{\ln(\Delta t_1/\Delta t_2)} = \frac{288.43 - 50}{\ln(288.43/50)} = 136°F$$

$$q = UA\Delta t_{1m}; \quad \text{Estimate } U = 200 \frac{BTU}{hr\cdot ft^2\cdot °F}$$

$$A = \frac{q}{U\ t_{1m}} = \frac{1,855,151}{200(136)} = 68.2\ ft^2$$

From Figure 14-28 [14] agitated falling-film evaporators (304ss)

Purchased cost = \$25,000 |246.8/109.7| = \$56,244

Installed cost = \$56,244 |1.39| = \$78,180

Volatiles - Product Storage Tank-- 4

Volatiles--

Organics = 269.1 lb/hr | ft^3/62.4 lb | 1/1.047 | = 4.12 ft^3/hr

Water = 1053.9 lb/hr | ft^3/62.4 lb | = 16.89 ft^3/hr

Total Volume = 21.01 ft^3/hr | 7.48 gal/ft^3 | = 157 gal/hr

Assume a 1 week capacity = 157 gal/hr | 24 hr/da | 7 da | = 26,400 gal

Use a tank volume of 26,000 gal (304ss)
From Figures 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = \$23,500 | 246.8/109.7 | = \$52,870

Installed cost = \$52,870 | 1.39 | = \$73,489

Extractor - 1st Stage-- 5

Vacuum Stripped Oil = 7677 lb/hr | ft^3/62.4 lb | 1/1.238 | hr/60 min | 65 min |

= 107.66 ft^3

Water = 13,183.2 lb/hr | ft^3/62.4 lb | hr/60 min | 65 min | = 228.88 ft^3

Use a residence time of 65 min.

Total volume = 336.53 ft^3

Use an extractor volume of 350 ft^3 (304ss)

From Reference [21] : $V = \frac{\pi}{4} d^2 h$

where h is assumed to be 20 feet

$350 \ ft^3 = (\pi/4) d^2 (20)$

d = 4.72 ft or 56.64 inches

From Figure 10 [21] - Cost of columns:

Purchased cost = \$51,000 | 0.8 | 246.8/180 | = \$55,941

The factor given for converting from a 316ss column to a 304ss column is 0.8.

Installed cost = \$55,941 | 1.39 | = \$77,758

Water Storage Tank-- 6

Water = 13,183.2 lb/hr |ft^3/62.4 lb| = 211.27 ft^3/hr

Capacity = 211.27 ft^3/hr |7.48 gal/ft^3| = 1580 gal/hr

Assume a 3 day supply = 1580 gal/hr |24 hr/da |3 da| = 113,781 gal

Use a tank volume of 110,000 gal (C-S)

From Figures 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = $15,000 |246.8/109.7| = $33,747

Installed cost = $33,747 |1.39| = $46,908

MIBK Storage tank-- 7

MIBK = 6248.2 lb/hr |ft^3/62.4 lb |1/0.801| = 125.01 ft^3/hr

Capacity = 125.01 ft^3/hr |7.48 gal/ft^3| = 935 gal/hr

Assume a 1% loss of MIBK in system through pumps, leakage, etc., which requires makeup.

Assume a two week supply = 935 gal/hr |24 hr/da |14 da |.01| = 3142 gal

Use a tank volume of 3500 gal (C-S)
From Figures 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = $2400 |246.8/109.7| = $5400

Installed cost = $5400 |1.39| = $7505

Spent Oil Storage Tank-- 8

Insoluble Oil Phase

Organics = 4238.2 lb/hr |ft^3/62.4 lb |1/1.235| = 55 ft^3/hr

Water = 1021.1 lb/hr |ft^3/62.4 lb| = 16.36 ft^3/hr

Total Capacity = 71.36 ft^3/hr |7.48 gal/ft^3|= 533.77 gal/hr

Assume a one week capacity = 533.77 gal/hr |24 hr/da |7/da| = 89,673 gal

Use a tank volume of 90,000 gal (304ss)
From Figures 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = $44,600 |246.8/109.7| = $100,340

Installed cost = $100,340 |1.39| = 139,472

Holdup Tank-- 9

Aqueous Phase = 15,600.9 lb/hr | ft^3/62.4 lb | 1/1.235| = 202.44 ft^3/hr

Capacity = 202.44 ft^3/hr | 7.48 gal/ft^3| = 1514.3 gal/hr

Choose a 4 hour Holdup = 6057 gal

Use a tank volume of 600 gal (308ss)

From Figures 13-56 [14] (Cost of mixing, storage, and pressure tanks:

Purchased cost = \$11,500 | 246.8/109.7| = \$25,872

Installed cost = \$25,872 | 1.39| = \$35,963

Extractor - 2nd Stage-- 10

Aqueous Phase = 15,600.9 lb/hr | ft^3/62.4 lb | 1/1.235 | hr/60 min | 65 min|

= 219.31 ft

MIBK = 6248.2 lb/hr | ft^3/62.4 lb | 1/0.801 | hr/60 min | 65 min| = 135.43 ft^3

Use a residence time of 65 min

Total volume = 354.74 ft^3

Use an extractor volume of 375 ft^3 (304ss)

From Reference [21] : $V = (\pi/4)d^2h$

where h is assumed to be 20 feet

$$375 \text{ ft}^3 = (\pi/4)d^2(20)$$

$$d = 4.89 \text{ ft or } 58.63 \text{ inches}$$

From Figure 10 [21] - Cost of columns:

Purchased cost = \$53,000 | 0.8 | 246.8/180| = \$58,135

The factor given for converting from a 316ss column to a 304ss column is 0.8.

Installed cost = \$58,135 | 1.39| = \$80,808

MIBK Soluble - Holdup Tank-- 11

MIBK = 6248.2 lb/hr | ft^3/62.4 lb | 1/0.801| = 125.01 ft^3/hr

Organics = 565 lb/hr | ft^3/62.4 lb | 1/1.235| = 7.33 ft^3/hr

Capacity = 132.34 ft^3/hr |7.48 gal/ft^3| = 990 gal/hr

Choose a 4 hour Holdup = 3960 gal

Use a tank volume of 4000 gal (304ss)

From Figure 13- 56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = \$9,000 |246.8/109.7 | = \$20,248

Installed cost = \$20,248 |1.39| = \$28,145

Evaporator (MIBK Phase)-- 12

Heat Requirements-- q = 1,082,907 BTU/hr

$$\Delta t_1 = (244 - 70)°F \quad \Delta t_2 = (358.43 - 249)°F$$

$$\Delta t_{1m} = \frac{\Delta t_1 - \Delta t_2}{\ln(\Delta t_1/\Delta t_2)} = \frac{174 - 109.43}{\ln(174/109.43)} = 139°F$$

$$q = UA\Delta t_{1m}; \quad \text{Estimate } U = 200 \frac{BTU}{hr \cdot ft^2 \cdot °F}$$

$$A = \frac{a}{U\Delta t_{1m}} = \frac{1,082,907}{200(139)} = 38.95\ ft^2$$

From Figures 14-28 [14] agitated falling film evaporators:

Purchased cost = \$16,500 |246.8/109.7| = \$37,121

Installed cost = \$37,121 |1.39| = \$51,599

MIBK Holdup Tank-- 13

MIBK = 6248.2 lb/hr |ft^3/62.4 lb |1/0.801| = 125.01 ft^3/hr

Capacity = 125.01 ft^3/hr |7.48 gal/ft^3| = 935.1 gal/hr

Choose a 4 hour Holdup = 3740 gal

Use a tank volume of 4000 gal (304ss)

From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = \$9,000 |246.8/109.7| = \$20,248

Installed cost = \$20,248 |1.39| = \$28,145

MIBK Soluble - Product Storage Tank-- 14

MIBK Soluble Organics = 565 lb/hr |ft^3/62.4 lb |1/1.235| = 7.33 ft^3/hr

Capacity = 7.33 ft^3/hr |7.48 gal/ft^3| = 54.8 gal/hr

Assume 1 week capacity = 54.8 gal/hr |24 hr/da | 7 da/wk| = 9211 gal

Use a tank volume of 9,000 gal (304ss)

From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = \$12,500 |246.8/109.7| = \$28,122

Installed cost = \$28,122 | 1.39| = \$39,090

Water Soluble - Holdup Tank-- 15

Water = 12,162.1 lb/hr $|ft^3/62.4\ lb|$ = 194.9 ft^3/hr

Organics = 2873.8 lb/hr $|ft^3/62.4\ lb|$ 1/1.235| = 37.29 ft^3/hr

Capacity = 232.2 ft^3/hr $|7.48\ gal/ft^3|$ = 1736.8 gal/hr

Choose a 4 hour Holdup = 6947 gal

Use a tank volume of 7,000 gal (304ss)

From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = \$11,800 |246.8/109.7| = \$26,547

Installed cost = \$26,547 |1.39| = \$36,901

Vacuum Evaporator-- 16

Heat Requirements -- q = 13,569,548 BTU/hr

$$\Delta t_1 = (220 - 70)°F \qquad \Delta t_2 = (358.43 - 220)°F$$

$$\Delta t_{1m} = \frac{\Delta t_1 - \Delta t_2}{\ln(\Delta t_1/\Delta t_2)} = \frac{150 - 138.43}{\ln(150/138.43)} = 144°F$$

$$q = UA\Delta t_{1m}; \quad \text{Estimate } U = 500 \frac{BTU}{hr\cdot ft^2\cdot °F}$$

$$A = q/U\Delta T_{1m} = 13{,}569{,}548/500(144) = 188.46\ ft^2$$

From Figure 14-28 [14] agitated falling-film evaporators

Purchased cost = \$48,000 |246.8/109.7| = \$107,989

Installed cost = \$107,989 |1.39| = \$150,105

Water Soluble - Product Storage Tank-- 17

Water Soluble Organics = 2873.8 lb/hr $|ft^3/62.4\ lb$ |1/1.235| = 37.29 ft^3/hr

Capacity = 37.29 ft^3/hr | 7.48 gal/ft^3 | = 279 gal/hr

Assumg a 1 week capacity = 279 gal/hr | 24 hr/da | 7 da/wk | = 46,860 gal

Use a tank volume of 50,000 gal (304ss)

From Figure 13-56 [14] Cost of mixing, storage, and pressure tanks:

Purchased cost = $32,300 | 246.8/109.7 | = $72,668

Installed cost = $72,668 | 1.39 | = $101,008

APPENDIX D

PHYSICAL PROPERTIES

TABLE D-1. TYPICAL VOLATILES ANALYSIS*

Component	Weight Per cent
Water	68.24
Acetic Acid	20.48
Methanol	1.70
Furfural	2.00
Formic Acid	2.42
Propionic Acid	0.60
Unknown	4.56

*Experimental Results

TABLE D-2. HEAT CAPACITY ESTIMATION* - VOLATILES

Component	(A) Weight Per cent	(B) cp $\frac{\text{BTU}}{\text{lb} \cdot {}^{\circ}\text{F}}$	(A) * (B)
Water	68.24	1.00	0.6824
Acetic Acid	20.48	0.522	0.1069
Methanol	1.70	0.590	0.0100
Furfural	2.00	0.416	0.0083
Formic Acid	2.42	0.524	0.0127
Propionic Acid	0.60	0.560	0.0034
Unknown	4.56	0.50 (Est.)	0.0228
cp - Weighted Average =			0.8465

* [15] Table 3-176 Specific Heats of Organic Liquids

TABLE D-3. HEAT CAPACITY ESTIMATION--VOLATILES LESS WATER

Component	grams*	(C) cp $\frac{\text{BTU}}{\text{lb} \cdot {}^\circ\text{F}}$	(D) Weight Fraction	(C) * (D)
Methanol	1.4	0.590	0.0534	0.0315
Formic Acid	2.0	0.524	0.0763	0.0400
Acetic Acid	16.9	0.522	0.6450	0.3367
Propionic Acid	0.5	0.560	0.0191	0.0107
Furfural	1.65	0.416	0.0630	0.0262
Unknown	3.75	0.50 (Est.)	0.1431	0.0716
Total	26.2			

cp - weighted average = 0.5167

*Experimental Results

TABLE D-4. DENSITY ESTIMATION--VOLATILES LESS WATER

Component	(A) Weight Fraction	(B) Density g/ml	(A) * (B)
Acetic Acid	0.6450	1.0491	0.6767
Methanol	0.0534	0.7914	0.0423
Furfural	0.0630	1.1598	0.0731
Formic Acid	0.0763	1.220	0.0931
Propionic Acid	0.0191	0.992	0.0189
Unknown	0.1431	1.00 (Est.)	0.1431

Density (ρ) - Weighted Average = 1.0472

TABLE D-5. HEAT OF VAPORIZATION* ESTIMATION--VOLATILES LESS WATER

	Boiling	Heat of Vaporization		Weight	
Component	Point-°C	cal/g	BTU/lb	Per cent	
Acetic Acid	118.3	96.8	174.24	0.6450	112.3848
Methanol	64.7	262.8	473.04	0.0534	25.2603
Furfural	60.5	107.5	193.5	0.0630	12.1905
Formic Acid	101	120	216.0	0.0763	16.4808
Propionic Acid	139.5	98.8	177.84	0.0191	3.3967
Unknown	--	100 (Est)	180 (Est)	0.1431	25.7580

Heat of Vaporization - Weighted Average = 195.5 BTU/lb

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* [20] , pp. 9-85 -- 9.95

TABLE D-6. SPECIFIC HEATS OF VARIOUS ORGANIC COMPOUNDS*

Compound	Specific Heat $\frac{BTU}{lb \cdot {}^\circ F}$ or $\frac{CAL}{g \cdot {}^\circ F}$	Temperature Range (°C)
Methyl Ethyl Ketone	0.549	20 - 78°C
Methyl Isobutyl Ketone	0.459	20
Methyl Isopropyl Ketone	0.525	20 - 91
Methyl Hexyl Ketone	0.55	22 - 168
Water	1.0	15

* [20], pp. 9-133

TABLE D-7. HEAT OF VAPORIZATION OF VARIOUS ORGANIC COMPOUNDS*

Compound	Heat of Vaporization cal/gram	Temperature °C
Methyl Ethyl Ketone	106.0	78.2
Methyl Isopropyl Ketone	89.8	92
Methyl n-Butyl Ketone	82.4	127
Methyl n-Amyl Ketone	82.7	149.2
Methyl Hexyl Ketone	74.1	173
Water	539.55	100

* [20], pp. 9-91

TABLE D-8. PROPERTIES OF MIBK*

Molecular Weight	100.16
Density g/ml	0.801 @ 20°/40°
Melting Point	-84.7 °C
Boiling Range	117 - 119 °C
Solubility in Water	2g/100g Water at 20°C

* [20], pp. 7-54

GLOSSARY

dissolved organics: The nonvolatile material remaining after evaporation of solvent of a fraction or phase.

fraction: A solution or solid derived from extracting a phase (as defined below) with an immiscible solvent.

neutrals of high aromaticity (NHA): Compounds in the pyrolytic oils which are nonpolar and nonacidic and exhibit UV fluorescing and absorbing (254 nm) characteristics.

nonvolatile organics (NVO): The fraction of organic material remaining after vacuum stripping at approximately 2 mm Hg and ambient temperature which contains phenolics, polyhydroxy neutral compounds, and neutral compounds of high aromaticity.

organic volatiles: The organic volatiles is equal to the difference between the total volatiles and amount of water in the total volatiles.

phase: A solution or solid derived from the original pyrolytic oil sample by evaporation or extraction, e.g. volatile phase, aqueous phase, organic phase, insoluble tar.

phenolics: The class of acidic compounds which are titratable with methanolic potassium hydroxide in N,N-dimethyl formamide solvent, and identifications are confirmed by GC, LC, TLC and IR evidence.

polyhydroxy compounds: The class of nonacidic compounds which are very water soluble, produce a blue color with Orcinol reagent, which is a characteristic of sugars, and have RF values similar to those of known sugar on a TLC plate.

total volatiles: The total volatile material, including both water and organics, removed by vacuum stripping at approximately 2 mm Hg and ambient temperature.

organic volatiles: The organic volatiles is equal to the difference between the total volatiles and amount of water in the total volatiles.